XVI. *The Development of Pressure Waves during the Longitudinal Impact of Bars. By* W. A. PROWSE, *B.Sc., Ph.D., Lecturer in Physics in the University of Durham* *.

WHEN two bodies collide a system of waves of compression starts out from the point of contact, through each of the bodies; these return generally as waves of rarefaction, but in the meantime, except in a few instances, the pressure between the bodies has increased, and they remain in contact while further waves pass out until the total amplitude of the returning waves of rarefaction exceeds that of the waves of compression [1]. In this manner the stresses due to the impact are distributed, and when the circumstances are such that the time required for a " return journey " of one of the waves is short compared with the total time of contact the distribution of stress at any instant during the impact is very much what it would be if the bodies were steadily held together under the pressure then acting. The course of the collision is then chiefly controlled by the masses of the bodies and the geometrical shapes of the surfaces in contact : the theory of this type of collision has been worked out in detail by Hertz [2].

If, however, two perfectly flat-ended rods of the same

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length were to impinge longitudinally only one wave would be required to distribute the stress, and the time of contact would be that required by a longitudinal wave to traverse twice the length of either bar [3]. Owing to the difficulty of getting such plane-ended bars into perfect contact this type of impact has never been realized experimentally [4]. An approach to these conditions is obtained in the longitudinal impact of metal rods whose ends have been ground to a spherical form of definite radius, and numerous experiments on this type of collision have been made, notably by Sears [5] and by Wagstaff [6], both of whom used a ball end of constant radius for all their experiments.

The work described below was undertaken to determine how the geometrical character of the impinging surfaces affects this type of collision.

In the first experiments the duration of contact of bars of various lengths, impinging longitudinally, was determined for a series of different velocities of approach, the two bars in each experiment having the same linear dimensions.

Cylindrical rods of silver steel, diameter 5/8″, were used for all the experiments. The ends of these were turned to the required radius of curvature, which varied from 4·6 to 0·16 cm., were hardened by quenching, and ground accurately to the required size. Finally the surfaces were polished with rouge. To preserve exactly the same end-conditions throughout the original bars in each set of experiments were cut down in successive stages from 63·6 cm. to 49·6 cm., 35·6 cm., 17 cm., and finally 8·5 cm. with few exceptions.

An optical method was used for measuring the radius of the ball ends where this exceeded 0·5 cm., but for the two bars of smaller end radius it was considered that the accurate fitting of the ends to a gauge gave a more satisfactory value than the use of optical methods.

The general arrangement of the apparatus is shown in fig. 1, which is drawn approximately to scale and includes practically everything except the electrical mechanism of the various circuits.

The bars were slung from stout brackets by means of eight cords (four to each bar) each about six feet long, and so adjusted that each bar could move only parallel to its axis in a vertical plane, while the two bars were

exactly in line when at rest in the equilibrium position, and when in that position remained with their ends just in contact. For this purpose each cord was attached at its upper end to a spindle which could be rotated by

Fig. 1.
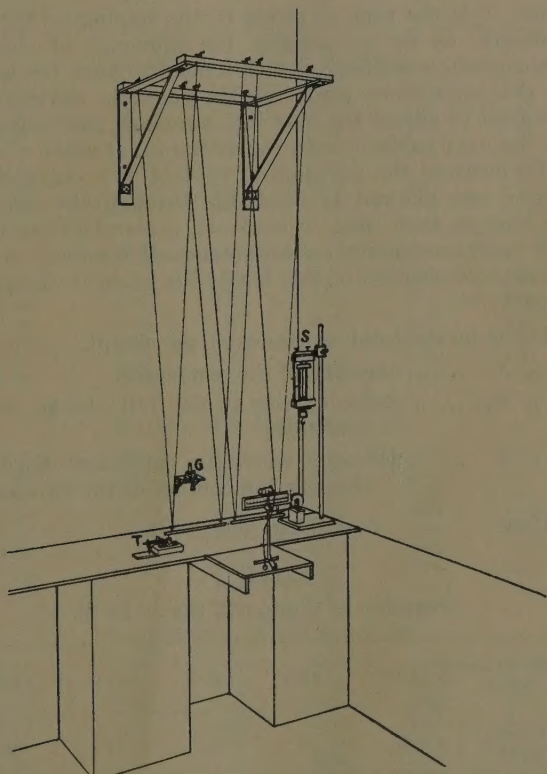
a worm wheel, so that a very delicate adjustment of the suspension was obtained. To the underside of each bar was attached a vertical metal pin, with an ebonite sleeve, for convenience in manipulation and to take the end of the fine wire used to make electrical connexion with the bar.

For each observation (on the time of contact) one of the bars was withdrawn a measured distance x, while the other remained stationary in the equilibrium position. On release the first bar struck the second with a velocity v given by

$$v = 2\pi x/\mathrm{T},$$

where T is the time of swing of the impinging bar. To eliminate as far as possible the influence of changing atmospheric conditions, which tended to alter the lengths of the suspension cords, electromagnetic devices were designed to adjust the bars into standard positions ready for the next collision with the minimum of delay.

To measure the duration of contact, t, a charged condenser was allowed to discharge through the two bars (so long as they were in contact), a standard resistance and a galvanometer of low inductance all in series. A more detailed description of this method is given in the papers cited [5], [6].

Let R be the total resistance of the circuit.

„ C   „   „ capacity of the condenser.

„ θ_0 „   „ deflexion due to the full charge on the condenser.

„ θ „   „ deflexion when the condenser discharges through the contact of the two bars.

Then $t = \mathrm{RC} \log_e (\theta/[\theta_0 - \theta]).$

Table I.
Duration of Contact, t (sec. $\times 10^{-4}$).

Length of bars (cm.).	63·6	49·6	35·6	17·0	8·5
Velocity (cm./sec.).	t.	t.	t.	t.	t.

Radius of ball end 4·60 cm.

2·18	4·67	4·13	3·45	2·47	1·88
3·27	4·44	3·72	3·26	2·24	..
4·36	4·23	3·69	3·11	2·12	1·59
6·45	4·03	3·46	2·89	1·97	..
8·73	3·88	3·31	2·74	1·87	1·36
13·09	3·74	3·09	2·57	1·71	1·25
17·45	3·54	2·95	2·45	1·62	1·16
24·00	3·39	2·86	2·31	1·53	1·08

TABLE I. (*cont.*).

Length of bars (cm.).	63·6	49·6	35·6	17·0	8·5
Velocity (cm./sec.).	*t.*	*t.*	*l.*	*t.*	*t,*

Radius of ball end 2·58 cm.

2·18	5·05	4·03	3·60	2·51	1·73
3·27	..	3·78	3·37	2·32	1·63
4·36	4·37	3·65	3·20	2·18	1·60
8·73	3·99	3·26	2·85	1·91	1·40
13·09	3·77	3·14	2·67	1·76	1·29
17·45	3·65	2·96	2·54	1·67	1·25
24·00	3·50	2·87	2·37	..	1·16

Radius of ball end 1·44 cm.

2·18	5·43	4·83	4·10	2·89	2·13
4·36	4·77	4·28	3·50	2·57	1·88
8·73	4·38	3·83	3·11	2·21	1·61
13·09	4·07	3·55	..	2·05	1·47
17·45	3·90	3·42	2·80	1·93	1·37
26·17	3·70	3·15	2·62	1·78	1·31

Radius of ball end 0·98 cm.

2·18	5·65	5·10	4·21	3·22	2·38
3·27	5·31	4·68	3·92	2·82	2·19
4·36	5·06	4·48	3·74	2·73	2·07
6·54	4·74	4·24	3·47	2·48	1·86
8·73	4·55	4·06	3·30	2·33	1·76
13·09	4·25	3·80	3·09	2·16	1·63
17·45	4·01	3·58	2·99	2·04	1·52
24·00	..	3·38	2·79	..	..

Radius of ball end 0·318 cm.

2·18	7·30	5·93	4·98	3·80	2·76
3·27	6·88	5·54	4·60	3·51	2·54
4·36	6·56	5·20	4·37	3·34	2·40
8·73	5·85	4·61	3·88	2·88	2·07
13·09	5·39	4·40	3·58	2·66	1·99
17·45	..	..	3·46	2·52	1·84
24·00	4·78	3·95	3·32	2·34	1·69

Radius of ball end 0·159 cm.

2·18	7·45	6·91	5·73	4·12	3·02
3·27	..	6·39	5·22	3·78	2·78
4·36	..	6·03	4·96	3·56	2·64
6·54	5·99	5·55	4·62	3·27	2·43
8·73	5·68	5·27	4·37	3·08	2·29
13·09	..	4·81	4·03	2·84	2·13
17·45	4·89	4·55	3·81	2·69	2·02

$\mathrm{Log}_{10} (\theta/[\theta_0-\theta])$ was plotted against $10^6/\mathrm{R}$ for five different series resistances, and from the slope of this graph, which was linear except during the deformation of the ends of soft-ended bars, the time of contact was calculated. A determination of the inductance of the galvanometer showed that this was small enough to be neglected.

In agreement with Wagstaff's results it was found that the relation between the time of contact and the velocity of approach could in all cases be represented by the equation

$$t = \mathrm{A}v^\gamma, \quad \ldots \ldots \quad (1)$$

where A and γ are constants independent of the velocity of approach.

From theoretical considerations Hertz [2] showed that the pressure P between two elastic bodies should be given by

$$\mathrm{P} = k_2\alpha^{3/2}, \quad \ldots \ldots \quad (2)$$

where k_2 is a function of the elastic properties of the bodies and of the principal curvatures of the surfaces in contact and α is the total indentation, *i. e.*, if the distance between two points remote from the region of contact, but on the normal to the area of contact, is x when the bodies just touch, it is $x-\alpha$ when the pressure is $\mathrm{P}.\alpha$, which is thus the sum of the indentations of both bodies, and will be referred to throughout as the total indentation. When the impact is slow, in the sense that the time of contact is long compared with the period of the gravest natural oscillations of either body, t can be determined by direct integration of equation (2), giving

$$t = 2 \cdot 943(5/4k_1k_2)^{2/5}.v^{-1/5},$$

where $k_1 = (m_1+m_2)/m_1m_2$, m_1 and m_2 being the masses of the colliding bodies.

On the other hand, when two ideal flat-ended bars of the same length and material impinge longitudinally the time of contact is simply $2.l/\mathrm{U}$, where l is the length of either bar and U the velocity of sound in the material. Any dependence of the time of contact on the velocity of approach thus suggests the application of the Hertz theory, more particularly when the form is that of equation (1). Since a value of zero for γ would indicate a time of contact independent of the velocity of approach,

i. e. (if the St.-Venant theory applies at all) dependent simply on longitudinal oscillations in the bar, the value of γ may be expected to throw some light on the relative importance of longitudinal waves in determining the time of contact.

TABLE II.

Values of $-1/\gamma$.

Length of bar (cm.).	63·6	49·6	35·6	17·0	8·5	
Radius of ball end (cm.).	$-1/\gamma$.	$-1/\gamma$.	$-1/\gamma$.	$-1/\gamma$.	$-1/\gamma$.	Inter-cept.
4·60	7·51	6·22	5·89	5·06	4·38	4·26
2·58	7·33	6·72	5·97	5·10	5·28	4·42
1·44	6·87	5·91	5·64	5·12	4·90	4·58
0·98	6·30	6·24	5·77	4·99	4·65	4·34
0·318	5·68	5·99	5·68	4·99	4·67	4·43

The following results are from unpublished experiments by J. E. P. Wagstaff :—

Length of bar (cm.).	63·6	49·6	35·6	17·0
Radius of ball end (cm.).	$-1/\gamma$.	$-1/\gamma$.	$-1/\gamma$.	$-1/\gamma$.
5·08	..	..	5·40	4·61
2·54	..	..	5·68	5·01
0·635	6·10	5·94	5·56	5·18

For all of the bars, except those of end radius 0·158 cm., which are discussed later, $-1/\gamma$ was found to be a linear function of the length. Further, the intercepts of each of these curves on the axis $l=0$ was the same for all of the bars within the limits of experimental error.

The impact of very short bars conforms to the conditions necessary for the application of the Hertz theory, and indeed the constant intercept referred to supports this

view except for the numerical value. Also the increase
of $-1/\gamma$ with l is to be expected if longitudinal waves
play an increasing part in the processes of collision for
longer bars. The hypothesis is therefore made that the
impact of short bars proceeds in general accordance with
the Hertz theory with some modification to account for
a change from $-1/5$ to $-1/4\cdot41$ in the value of γ.

Before discussing possible theoretical interpretations
of these results the omission of the values of γ for the
most pointed bars should be explained. The chief
sources of error during the experiments were the occasional
deposit of specks of dust on the ball ends and the possible
change in length of the suspension cords : if only one
of the cords stretched, for instance, the alignment of the
bars would be spoilt. Discrepancies due to dust were
easily recognized by sudden inconsistencies in the galvano-

TABLE III.

Radius of ball end (cm.)	0·158	0·318	0·98	1·44	2·58	4·60
Error (per cent.) ..	8	1·7	0·4	0·1	0·03	0·01

meter readings, and the set of observations was then
repeated. On the basis of these repetitions it is considered
that the accuracy of the readings in Table I., many of
which are the mean of two sets of observations, is within
2 per cent. for the lowest velocity and within 1 per cent.
for the remainder, except for the bars of end radius
0·158 cm.

Errors due to changes in length of the cords would be
most serious where the precision of the alignment was
most important, $i.\ e.$, for the most pointed bars. With
these, repetitions of series of observations showed dis-
crepancies of the order of 8 per cent., despite great care
in working and the absence of inconsistencies within
any one series. Assuming that this difficulty was due
to changes in alignment, the lateral displacement of one
of the bars necessary to produce the observed error was
calculated, and hence the corresponding error for the other
bars (Table III.).

After completion of the observations recorded in Table I. an earnest attempt was made to obtain a reliable series of values of γ for new bars of end radius 0·158 cm., but no consistent results were obtained.

It appeared possible that for the large stresses set up during impact the relation between P and α deduced by Hertz might not hold exactly, but that P might be proportional to α^β where β is not exactly 1·5. Some support is afforded to this suggestion by the work of Lafay[7], who measured, by an interferometer method, the indentation produced when a steel sphere was pressed against a steel block. The values of β calculated from his results are given in Table IV.

TABLE IV.

Radius of sphere (cm.)	0·5	1·0	2·0	3·0	6·0	15·0	25·0
β	1·64	1·64	1·64	1·68	1·63	1·97	2·07

The greatest radius of curvature used in the experiments described in this paper was 4·60 cm. It will be seen that the values of β expressed in the above table are sensibly constant over this range, the mean being 1·646, which corresponds, according to the theory outlined below, with a value $-1/4\cdot10$ for γ.

In the equation

$$P = k_2 \alpha^\beta \qquad \ldots \ldots (4)$$

P may be replaced by the rate of change of momentum giving

$$d^2\alpha/dt^2 = -k_1 k_2 \alpha^\beta.$$

On integration this gives

$$v^2 = \frac{2k_1 k_2 \alpha_1^{\beta+1}}{\beta+1}.$$

k_2 can be reduced to the form

$$k_2 = \frac{\sqrt{2}}{3} r^{\frac12} U^2 \rho \frac{1-2\sigma}{(1-\sigma)^2}$$

when the impinging surfaces are spherical, of the same radius r, and of the same material.

U=the velocity of sound in the steel used,

ρ=the density of the material,

σ=Poisson's ratio for the material.

Substituting for k_1, and considering the case of equal cylindrical bars, of radius 5/16″ of steel for which $\sigma = 1/4$, $U = 4 \cdot 908 \times 10^5$ cm./sec. ; the following result is obtained :

$$1/k_1 k_2 = \cdot 943 \times 10^{-11} l r^{\frac{4}{5}},$$

where l represents the length of either bar and r the radius of the ball end.

The expression for the duration of contact can now be written

$$t = v^\gamma l^{\frac{1+\gamma}{2}} r^{-\frac{1+\gamma}{4}} \cdot \psi, \quad \ldots \quad (5)$$

where

$$\psi = \sqrt{\pi} \frac{\sqrt{\dfrac{1+\gamma}{2}}}{\sqrt{\dfrac{2+\gamma}{2}}} (1+\gamma)^{\frac{1-\gamma}{2}} (\cdot 943 \times 10^{-11})^{\frac{1+\gamma}{2}}.$$

Table V.

$-1/\gamma$	4·0	4·5	5·0	5·5	6·0	6·5	7·0
$\psi \times 10^4$	2·37	1·66	1·25	0·99	0·81	0·69	0·60

Two possibilities present themselves, that the variation of γ with l is associated with a variation of β with the conditions of impact, and, alternatively, that β remains constant and is a characteristic property of the ball ends for all circumstances. Calculations of t based on equation (5) showed that the variation of ψ with γ was so rapid as to produce a considerable discrepancy between the calculated and observed variation of t with l. Accordingly it is considered that β remains constant, or reasonably so, throughout, with a characteristic value determined by the conditions for which the Hertz theory applies most closely, namely, that $l = 0$:

$$\beta = 1 \cdot 586.$$

The elastic properties of steel wire subject to great stresses of short duration have been examined by B.

Hopkinson[8], who found that Hooke's law applied over a much greater range than for static loads. If this be true for the bars used in these experiments the alteration of β from 1·5 is to be sought rather in the nature of the materials used than in a failure of the elastic theory. The ball ends of the bars after heat treatment consist of a core of steel, probably still fairly malleable and certainly not completely hardened, surrounded by a shell of glass-hard steel whose elastic properties (particularly Young's modulus and Poisson's ratio) might differ appreciably from those of the rest of the bar. It is therefore suggested that for very short bars the Hertz theory applies in its original form, and that the apparent disagreement between experiment and theory is due to a variation of k_2 with the depth to which the intense local stresses penetrate, *i. e.*, with α. Lafay's results were very probably obtained with case-hardened steel, and so may be expected to fall into the same category.

The effect of the length of the impinging bars, besides appearing in the value of γ, is directly manifested in a variation of t with l. This variation, however, was of no simple form, agreeing neither with the Hertz theory (wherein l would affect only the mass of the bars) nor with the St.-Venant theory, in that the graph of t against l was not linear nor was there any definite similarity in form among these curves for the bars of different end radii.

This is in marked contrast with the results obtained by Sears, who found that for bars of 1″ end radius and length greater than about 14 cm. the time of contact was a linear function of the length. Here again the importance of the physical state of the impinging surfaces is indicated, for the ends of Sears's bars were not hardened. To examine in greater detail the effects associated with the hardening of the ends a new series of experiments was begun, using two separate pairs of bars identical except in that the ball ends of one pair were not hardened while the ends of the other pair were finished as usual. These bars are referred to as '' soft-ended '' and '' hard-ended '' respectively. A considerably greater range of velocities was used in these new experiments (Tables VII. and VIII.).

At the conclusion of the earlier experiments (Table I.) a series of photomicrographs at a low magnification ($\times 38$)

of the polished ends was made to see whether the high local pressures developed during the collisions had produced any permanent indentation or other damage. No such deformation was observed, but on the ends of the bars a system of minute scratches appeared which, from their orientation, had been produced when the bars were swinging gently in contact during adjustments of the apparatus. This was avoided during subsequent work by protecting the ball ends with a cap of metal foil until adjustments were completed.

TABLE VI.

Diameter of Circle of Contact, D (10^{-2} cm.).

Length of bars 8·5 cm. throughout.		
Velocity (cm./sec.).	Radius of ball end (cm.).	D.
13·09	4·60	7·8
13·09	1·44	4·7
2·18	0·98	2·0
4·36	0·98	2·2
8·73	0·98	2·9
13·09	0·98	3·6
18·54	0·98	4·7
13·09	0·159	2·1

Partly to test the sphericity of the ball ends, but chiefly to see whether it would be possible to determine the area of contact in future experiments, one of the ball ends of a pair was lightly sooted before collision. An examination of an enlarged image of the sooted end now showed a clean circular patch, with a definite inner boundary closely surrounded by an outer concentric boundary. Repetitions of the experiment showed that the diameter of the inner ring depended only on the circumstances of the impact, while the distance between the two boundaries depended on the thickness of the layer of soot. The clearest results were obtained by using an ordinary wax taper and so light a coat of soot that the polish was scarcely dimmed.

Since observations on the area of contact might well lead to an experimental relation between β and γ, the new work on hard-ended bars was accompanied by a series of such determinations (Table IX.).

Measurements of the duration of contact of the soft-ended bars were made over the same range of velocities as for the hard-ended bars, but, owing to the deformation which occurred during the impacts, a somewhat modified

TABLE VII.

Time of Contact, t, hard-ended bars (10^{-4} sec.).

Radius of ball end 1·44 cm.

Length of bar (cm.).	.63·6	49·6	35·6	17·0
Velocity (cm./sec.).	t.	t.	t.	t.
0·44	6·85	6·04	5·47	4·02
0·65	6·43	5·64	5·08	3·60
0·87	6·29	5·40	4·76	3·50
1·31	5·81	5·11	4·45	3·21
2·18	5·37	4·56	4·04	2·87
3·27	5·05	4·26	3·65	2·64
4·36	4·84	4·08	3·57	2·54
6·54	4·49	3·85	. .	2·34
8·73	4·30	3·67	3·14	2·21
13·09	3·99	3·43	2·96	2·05
17·45	3·76	3·26	2·85	1·93
24·00	. .	. .	2·62	1·84

procedure was adopted. A withdrawal of 1 cm. was first used and a series of galvanometer readings taken. The deflexion suffered a gradual decrease as the ends of the bars were flattened, while the resilience, which had been poor during the deformation, became sensibly perfect. When this had happened a set of readings was taken as usual. This process was repeated for various displacements up to and including 11 cm. When the flattening was complete for this (the maximum) displacement an extended series of observations was begun as for the hard-ended bars. At the conclusion of each series it was found necessary to regrind the ball ends as flats of appreciable size had been produced by the collisions.

Both groups of results for soft-enderd bars, those taken before and those taken after the most violent impact,

failed to satisfy an expression of the type $t = Av^\gamma$, so that the simple relation expressing the behaviour of all hard-ended bars did not apply at all to soft-ended bars. The importance of the shape of the ends in determining the absolute value of t is clearly shown by the discrepancy between the values of t before and after the most violent

TABLE VIII.

Time of Contact, t, soft-ended bars (10^{-4} sec.).

Radius of ball end 1·44 cm.

Length of bar (cm.).	63·6	49·6	35·6	17·0
Velocity (cm./sec.).	t.	t.	t.	t.
2·18	5·05	4·33	4·01	2·84
4·36	4·31	3·94	3·42	2·41
8·73	3·73	3·48	3·02	2·11
17·45	3·38	3·07	2·61	1·84
24·00	3·26	2·88	2·43	1·69
0·436	5·57	5·05	4·96	3·45
0·654	5·31	4·75	4·44	3·25
0·873	5·10	4·58	4·13	3·08
1·31	4·75	4·27	3·80	2·84
2·18	4·36	3·99	3·45	2·54
4·36	3·89	3·58	3·10	2·23
6·54	3·69	3·35	2·93	2·11
8·73	3·56	3·22	2·82	1·99
13·09	3·44	3·06	2·65	1·85
17·45	3·34	2·96	2·54	1·74

impact, the slight flattening of the ends having the same effect as an increased radius of curvature.

For bars of length greater than about 30 cm. the time of contact was a linear function of the length for all but the smallest velocities of approach ($v > 1\cdot31$ cm./sec.). It appears then that the collisions of hard-ended and soft-ended bars are fundamentally different in type, so that the varying results obtained by different workers were only to be expected.

In agreement with this the results of the extended observations (Table VII.) on the hard-ended bars verified the complete applicability of the relation $t = Av^\gamma$ over the new range of velocities, and also gave values of γ in

good accord with the earlier observations. A very similar expression,

$$D = A'v^\delta, \quad \ldots \ldots \quad (7)$$

appeared to satisfy the relation between the diameter, D, of the circle of contact and the velocity of approach. A' and δ are independent of D and of v. Unfortunately the utility of this equation as a criterion of the applicability of the Hertz theory or of a suitable modification of that theory is small, because of the difficulty of obtaining

TABLE IX.

Diameter of Circle of Contact, D (10^{-2} cm.).

Hard-ended bars, radius of ball end 1·44 cm.

Length of bar (cm.).	63·6	49·6	35·6	17·0
Velocity (cm./sec.).	D.	D.	D.	D.
2·18	2·78	2·71	2·66	2·55
4·36	3·89	3·84	3·50	3·02
8·73	..	4·87	4·59	4·00
13·09	6·06	5·80	5·49	4·74
17·45	6·52	6·49	6·21	5·46

reliable values of D at small velocities. Although equation (7) gave values of δ very nearly 0·4, in accordance with the Hertz theory, these values could not be fixed with sufficient precision to distinguish between 1·50 and 1·59 as suitable values for β.

To examine the process of impact more closely it was decided to determine from the values of D the greatest pressure between the bars during the collisions : the calculation according to the Hertz theory presents no difficulty, but as the exact relation between P and α was still a matter of some doubt it was decided, at the conclusion of the timing experiments, to apply static pressures to the bars in contact and determine the corresponding values of D.

One of the bars (A, fig. 2) was firmly fixed with its axis vertical and its ball end downwards. The other was

held in a wooden frame, FF, as shown, which could be raised by tension applied through the cord C. To the
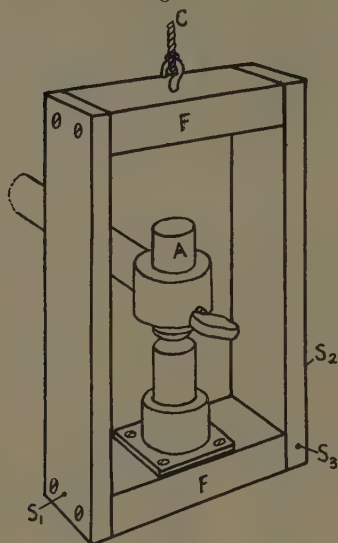
Fig. 2.

TABLE X.

Diameter of Circle of Contact, D (10^{-2} cm.).

Radius of ball end (cm.).	4·60	1·44	0·98	0·318
Load, P (dynes).	D.	D.	D.	D.
$1·47 \times 10^7$	7·22	4·07	3·22	··
0·981 ,,	5·22	3·76	3·12	2·14
0·491 ,,	4·17	2·64	2·24	1·76
0·196 ,,	3·22	1·97	1·53	1·18

lower part of the frame were attached three fine cords, S_1, S_2, S_3, fastened at their remote ends to spindles with worm-wheel adjustments. These cords were almost in

a horizontal plane, and by careful manipulation it was possible so to adjust them that the bars came just into contact and in correct alignment when a tension of 1 kg. weight was applied through C. The elasticity of the cords was sufficient for an extra load of a few grams to displace the suspended bar a few millimetres when the adjustment was nearly complete. When the bars had been brought into contact the required load was applied as an extra tension in C, after which the lower bar was removed to measure the diameter of the circle of contact.

Fig. 3.
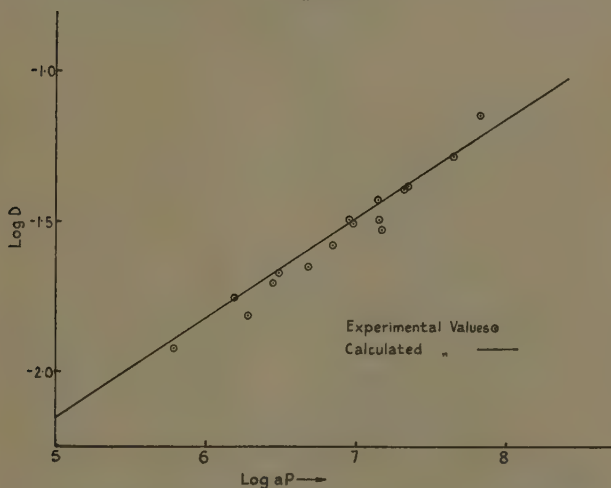
In equation (2) α is the total indentation and the indentation of either surface is $\alpha/2$. Further[9], the indentation at the edge of the circle of contact, is half that at the centre, so that the diameter of the circle of contact may be written

$$D = (2a\alpha)^{\frac{1}{2}}. \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Substituting in equation (2), and putting in the calculated value of k_2,

$$aP = 2.81 \times 10^{11}.D^3. \quad . \quad . \quad . \quad (9)$$

In fig. 3 the experimental points are plotted for comparison with this relation, which is expressed by the

straight line. The points provide no evidence for a value of β greater than 1·5, but do show that if β is assumed to be 1·586 the constant k_2 of equation (4) cannot have the value calculated from the elastic constants of the material. For further calculations the choice lies between starting with equation (4), using the experimental value of k_2, and starting with equation (2), using the calculated value, which, with this equation, agrees reasonably well with experiment. Since the deviation of γ from $-1/5$ when $l=0$ is considered to represent the effect of a small change of k_2 with α, and since the experimental error does not allow the constant of equation (4) to be determined with

Fig. 4.
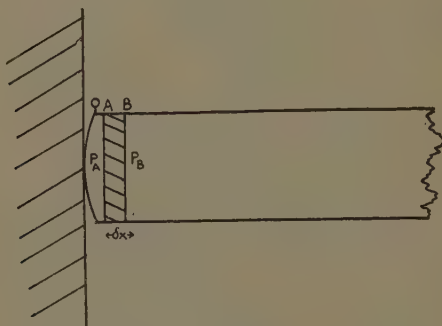
any precision, the remaining calculations are based on equation (2).

To examine in detail the course of a collision, consider the impact of two bars each of infinite length and moving towards one another each with the same velocity. When the ends come into contact, by the symmetry of the system, the surface of separation remains plane and stationary, and the problem becomes that of the impact of a round-ended elastic rod with a perfectly rigid plane. As soon as the ball end touches the plane a wave of compression proceeds along the rod, with the velocity of sound in the material of the rod, in which the condensation reflects exactly the increase of pressure on the ball end with time. It is useful to determine how this pressure will grow.

Since the stresses due to the indentation of the ball end fall off very rapidly with distance a section of the bar close to the ball end may be considered to be subject to a distributed total pressure P_a over one face and a similar pressure P_b over the other, while at the same time the displacement of the centre of the section from its position when the end is just in contact with the plane is $\alpha/2$. The displacements at P_a and P_b respectively may be written $\frac{1}{2}\left(\alpha + \frac{\delta\alpha}{2}\right)$ and $\frac{1}{2}\left(\alpha - \frac{\delta\alpha}{2}\right)$, where $\delta\alpha$ is the increase in the total indentation α during the time δt required for a wave of compression to travel from A to B, a distance δx.

Then, from equation (2),

$$P_a - P_b = (3/2)k_2\alpha^{\frac{1}{2}}\delta\alpha,$$

and if U be the velocity of sound in the bar, since $AB = U\delta t$,

$$P_a - P_b + \frac{\ddot{\alpha}}{2}\rho U\delta t = 0.$$

On integration this gives

$$\frac{\rho U}{2}\alpha_1^{-\frac{1}{4}}\int_{y=0}^{y=\alpha/\alpha_1}\frac{dy}{1-y^{3/2}} = k_2 t, \quad . \quad . \quad (10)$$

where t is the time which has elapsed since the beginning of the impact, α_1 is the value of α when the section has become stationary, *i. e.*, corresponding to the passage of a wave of constant amplitude down the bar, as in the St.-Venant theory, and $y = \frac{\alpha}{\alpha_1}$ at any instant.

The value of this integral between various limits from 0 to 1 has been computed graphically. For two instants t and t' during one collision the corresponding indentations α and α' are related by the expression

$$\frac{t}{t'} = \int_{y=0}^{y=\alpha/\alpha_1}\frac{dy}{1-y^{3/2}}\bigg/\int_{y=0}^{y=\alpha'/\alpha_1}\frac{dy}{1-y^{3/2}},$$

from which the relative values of $\frac{\alpha}{\alpha_1}$ and $\frac{\alpha'}{\alpha_1}$ may be found. The corresponding values of the pressure, expressed as a fraction of the limiting pressure, are set forth in fig. 5. $\int_0^1\frac{dy}{1-y^{3/2}}$ is infinite, indicating an asymptotic approach to

the final pressure, so the time taken for the pressure to reach 0·98 of its limiting value has been taken as standard. This choice is entirely arbitrary : the value of the fraction affects only the scale of the abscissæ, and no absolute measurements are made on this diagram.

An estimate may now be obtained of the nature of the errors intoduced by the assumption that the acceleration of the layer AB is $\ddot{\alpha}$. Suppose the section AB is initially at a distance x from the pole of the ball end. Then at an instant t after the beginning of the impact the distance of the section from the ball end is $x-(\alpha/2+i)$ where i expresses the decrease in length of the portion AO of the bar due to the condensation in the wave now passing

Fig. 5.
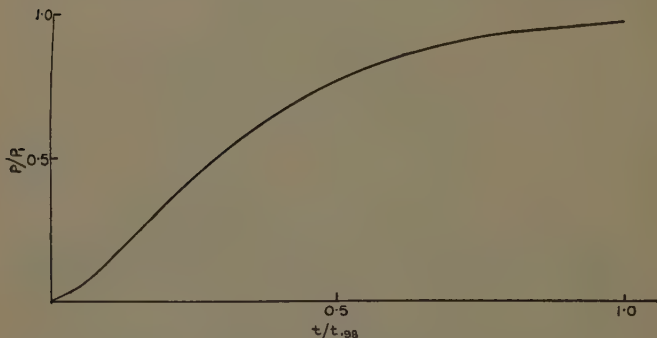
down the bar. i will be very nearly the reduction in the length OA caused by the pressure P applied to the end of the bar. Also $P=k_2\alpha^{3/2}$, so that $i=B\alpha^{3/2}$, where $B=k_2/AE$ and A=area of cross-section of the bar, E=Young's modulus.

The acceleration of the section is $\ddot{\xi}$, where $\xi=\alpha/2+B\alpha^{3/2}$;

$$\therefore \quad \ddot{\xi}-\frac{\ddot{\alpha}}{2}=-\frac{3}{4}B(2\alpha^{\frac{1}{2}}\ddot{\alpha}+\alpha^{-\frac{1}{2}}\dot{\alpha}^2{}_1).$$

The greatest correction arises when $r=4\cdot60$ cm. and $v=24\cdot0$ cm./sec. For a section 0·5 cm. from the end the effect of the corrections in this instance is shown in fig. 6, in which the upper curve gives $\ddot{\alpha}$ and the dotted curve $2\ddot{\xi}$. These results were obtained by plotting α against t, on

the basis of the uncorrected equations, and deducing graphically the values of $\dot{\alpha}$ and $\ddot{\alpha}$. It will be seen that in this, the least favourable instance, the corrections are of the same order as the experimental error ; further, a distance as great as 0·5 cm. is not contemplated in the theory for a ball end of this large radius.

During the collision of bars of finite length the pressure wave will grow in the manner described until the return of the wave, now of expansion, reflected from the free ends of the bars, *i. e.*, until a time $2l/U$ from the first

Fig. 6.
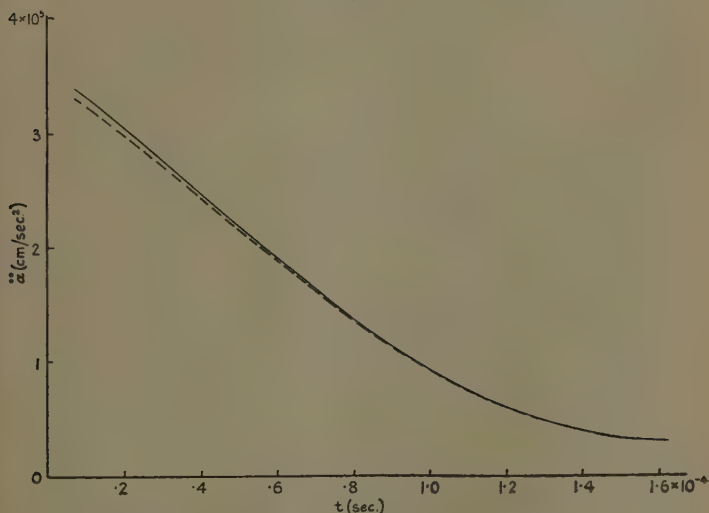
contact. The initial wave now returns to the ball end as a rarefaction, so that the pressure begins to decrease. Suppose now that at the ball end, the end of the bar being fixed, the wave of expansion is reflected as at a " closed end," then twice the original rarefaction must be added to the growing pressure. The actual nature of this reflexion is discussed below.

The course of the pressure variations is shown in fig. 7, where A represents the beginning of the impact. From A to B the pressure grows steadily, and would continue so to grow but for the reflected wave reaching the ball

end when twice the condensation of the corresponding point on the curve AB (given by the curve CD) must be deducted from the continuation, BE, of the pressure curve. The resultant decrease of pressure is represented by BF. It will be seen that if CB is nearly equal to the limiting pressure, CF will represent the time required for AB to reach half the pressure GF. The duration of contact is thus $2.l/U+$(time required for pressure to reach half its greatest value) in the simplest case.

In support of this it will be seen that for bars of end-radius 1·44 cm. there is only a small change in the greatest

Fig. 7.

pressure from $l=63·6$ cm. to $l=35·6$ cm. for the higher velocities of approach, indicating that the limiting pressure has nearly been attained, and that in this range $t-2.l/U$ is sensibly independent of the length of the bars (Table XIII.).

The reflexion of a sound wave at the interface between two media is governed by the boundary conditions, but the sum of all the changes which are likely to be introduced into the wave may be expressed as a change of amplitude together with a change of phase. Frequently, as in the reflexion of the pressure wave at the free end of these bars, the conditions are simple enough for the changes to be directly evident, but the ball end presents more

complicated conditions. The pole of the ball end is stationary. and, alone, would reflect in the same way as the closed end of an organ-pipe ; alternatively it can be considered that the compression wave in either bar would, if the contact were perfect, pass straight through into the other bar. Some part of the returning energy, however, will travel down the outer layers of the bar, and at the ball end will be reflected from the outer zones of the end, which are not fixed like the pole, but are restrained by the rigidity of the material between the pole and the outer zones. It is evident that the ball end cannot be regarded as either a true free surface or as a completely constrained surface, and the possibility of phase and amplitude changes in the reflected wave must be borne in mind.

Such changes can be incorporated in the expression for the duration of contact by writing

$$t = 2 . l/\mathrm{U} + \delta t + \varDelta \mathrm{T}, \quad . \quad . \quad . \quad (11)$$

where δt is the displacement of the curve CD (fig. 7) along the time scale, due to a change of phase in the reflected wave, and $\varDelta \mathrm{T}$ is the time required for the pressure curve to grow to some fraction (not necessarily one-half) of its final value. Where the time of contact is greater than $4 . l/\mathrm{U}$ and more than one reflexion at the ball end is involved the circumstances become more obscure, but if the reflexion at the ball end is imperfect, as suggested, the compression in a twice-reflected wave may well be fairly small, in which case the only alteration to (11) would be an extra correction for the phase change for each additional reflexion. Thus

$$t = 2 . l/\mathrm{U} + n \delta t + \varDelta \mathrm{T}, \quad . \quad . \quad . \quad (12)$$

where n is the number of reflexions at the ball end.

That this suggestion is not unreasonable is borne out by the conclusion to which it leads as to the distribution of energy : that in long bars and where $\varDelta \mathrm{T}$ is small a large part of the energy will exist in a longitudinal wave during the impact, but in short bars the energy in the waves is at each reflexion largely converted into strain-energy in the neighbourhood of the area of contact, resulting ultimately in the condition postulated by Hertz—that the strain is almost entirely confined to a small volume round the area of contact.

The method used to determine the value of δt and $\varDelta \mathrm{T}$ for a series of observations is illustrated in Table XI.,

in which the first part gives the values of $t-2.l/U$ and n (in brackets). This time, $t-2.l/U$, shows, for a given velocity of approach, a sudden change in value when

TABLE XI.

The number in brackets following the value of $t-2l/U$ indicates the number of reflexions at the ball end.

Radius of ball end 4·60 cm.

	$t-2l/U$ in sec. $\times 10^{-4}$.				
Length of bars (cm.).	63·6	49·6	35·6	17·0	8·5
Velocity (cm./sec.).	$t-2l/U$.	$t-2l/U$.	$t-2l/U$.	$t-2l/U$.	$t-2l/U$.
2·18	2·08 (1)	2·13 (1)	2·00 (2)	1·78 (3)	1·54 (5)
3·27	1·85 (1)	1·81 (1)	1·81 (1)	1·55 (3)	..
4·36	1·64 (1)	1·67 (1)	1·66 (1)	1·43 (3)	1·24 (4)
6·45	1·44 (1)	1·42 (1)	1·44 (1)	1·28 (2)	..
8·73	1·29 (1)	1·28 (1)	1·29 (1)	1·18 (2)	1·01 (3)
13·09	1·15 (1)	1·07 (1)	1·12 (1)	1·02 (2)	·90 (3)
17·45	·95 (1)	·93 (1)	1·00 (1)	·93 (2)	·82 (3)
24·00	·80 (1)	·83 (1)	·86 (1)	·84 (1)	·73 (2)

Mean correction for one reflexion $-0·13 \times 10^{-4}$ sec.

	Below, values of $\varDelta T$.				
					Mean.
2·18	2·21	2·26	2·26	2·17	2·19	2·22
3·27	1·98	1·94	1·94	1·94	..	1·95
4·36	1·77	1·80	1·79	1·82	1·76	1·79
6·45	1·57	1·55	1·57	1·54	..	1·56
8·73	1·42	1·41	1·42	1·44	1·40	1·42
13·09	1·28	1·20	1·25	1·28	1·29	1·26
17·45	1·08	1·06	1·13	1·19	1·21	1·13
24·00	·93	·96	·99	·97	·99	·97

n changes so that δt can be calculated, and is actually found to have a reasonably constant value throughout the table. A mean value of δt is now obtained, and $n\delta t$ is subtracted from $t-2 \cdot l/U$ to give the values of $\varDelta T$ shown in the second half of the table. It will be seen that δt is negative. The results of the same operation applied to the other bars are shown in Table XII.

TABLE XII.

Values of $\Delta T(10^{-4}$ sec.).

Length of bars (cm.).	63·6	49·6	35·6	17·0	8·5
Velocity (cm./sec.).	ΔT.	ΔT.	ΔT.	ΔT.	ΔT.

Radius of ball end 2·58 cm.

2·18	2·66	2·41	2·55	2·42	2·38
3·27	..	2·16	2·32	2·33	2·28
4·36	1·98	2·03	1·89	2·29	2·05
8·73	1·60	1·44	1·60	1·62	1·65
13·09	1·38	1·32	1·42	1·47	1·54
17·45	1·26	1·14	1·29	1·18	1·30
24·00	1·11	1·05	1·12	..	1·21

Radius of ball end 1·44 cm.

2·18	3·18	3·15	3·16	2·88	2·80
4·36	2·35	2·43	2·39	2·39	2·38
8·73	1·96	1·98	2·00	2·03	1·94
13·09	1·65	1·70	..	1·70	1·80
17·45	1·48	1·57	1·52	1·58	1·70
26·17	1·28	1·30	1·34	1·43	1·47

Radius of ball end 0·98 cm.

2·18	3·46	3·48	3·36	3·33	3·23
3·27	3·12	3·06	3·07	2·92	3·04
4·36	2·67	2·66	2·69	2·64	2·93
6·54	2·35	2·42	2·42	2·38	2·51
8·73	2·16	2·24	2·25	2·23	2·41
13·09	1·86	1·98	1·84	2·06	2·09
17·45	1·62	1·76	1·74	1·74	1·77
24·00	..	1·56	1·54	..	..

Radius of ball end 0·318 cm.

2·18	5·35	5·87	4·81	4·71	4·65
3·27	4·93	4·48	4·43	4·42	4·43
4·36	4·51	4·14	3·88	4·25	4·29
8·73	3·58	3·23	3·39	3·47	3·32
13·09	2·72	3·02	3·09	3·25	3·24
17·45	..	..	2·65	2·79	2·77
24·00	2·51	2·57	2·51	2·61	2·62

Radius of ball end 0·159 cm.

2·18	5·94	5·97	5·72	5·59	5·91
3·27	..	5·09	4·85	4·89	4·95
4·36	..	4·73	4·59	4·67	4·81
6·54	4·12	4·25	4·25	4·38	4·24
8·73	3·77	3·97	4·00	3·83	4·10
13·09	..	3·51	3·30	3·59	3·58
17·45	2·66	3·25	3·08	3·08	3·11

Equation (10) provides a means of calculating a theoretical value for the diameter of the circle of contact. Returning to the growth of a wave in a very long rod the conditions approximate to those of the St. Venant theory, and the greatest, or limiting, compression in the rod will be such as to cause a change of velocity v (the velocity of approach) for every part of the rod; the necessary pressure is $\rho v U/2$ *. From this

$$\alpha_1^{3/2} = \rho v U/(2k_2),$$

TABLE XIII.

l.	v.	N.	P/P_1.	D calc.	D obs.
63·6	17·45	2·66	0·963	$6·91 \times 10^{-2}$	$6·52 \times 10^{-2}$
49·6	17·45	2·07	0·908	6·78	6·49
35·6	17·45	1·49	0·795	6·48	6·21
17·0	17·45	0·710	0·435	5·30	5·46
63·6	13·09	2·42	0·945	$6·24 \times 10^{-2}$	$6·06 \times 10^{-2}$
49·6	13·09	1·88	0·881	6·09	5·80
35·6	13·09	1·35	0·751	5·78	5·49
17·0	13·09	0·646	0·394	4·66	4·74
63·6	8·73	2·11	0·914	$5·33 \times 10^{-2}$	$5·13 \times 10^{-2}$
49·6	8·73	1·65	0·834	5·23	4·87
35·6	8·73	1·18	0·686	4·90	4·59
17·0	8·73	0·565	0·334	3·86	4·00
63·6	4·36	1·675	0·842	$4·17 \times 10^{-2}$	$3·89 \times 10^{-2}$
49·6	4·36	1·306	0·734	3·98	3·84
35·6	4·36	0·937	0·571	3·66	3·50
17·0	4·36	0·448	0·253	2·79	3·02
63·6	2·18	1·330	0·742	$3·17 \times 10^{-2}$	$2·78 \times 10^{-2}$
49·6	2·18	1·037	0·622	2·99	2·71
35·6	2·18	0·744	0·457	2·70	2·66
17·0	2·18	0·356	0·189	2·01	2·55

which, substituting for ρ, U, and k_2, gives

$$N = t_1 \times 10^4 . (av)^{1/3} . /2·85,$$

where N is written for $\int_0^{\alpha/\alpha_1} \dfrac{dy}{1-y^{3/2}}$ and t_1 is the time during which the pressure wave grows without interference from the returning waves ,*i. e.*, $t_1 = 2.l/U$. Since N depends only on α/α_1, α and D can now be calculated (Table XIII.).

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* This result may also be obtained from equation (10) by substituting $\dot{\alpha} = v$ when $\alpha = 0$.

In fig. 7 the pressure rises to FG in a time t, the whole time of impact, so that the curve CD must rise to the same pressure in a time $\varDelta$T. Now CD is simply the first part of ABGE with the ordinates multiplied by some constant, say M. If AF' represent $\varDelta$T, then $M = GF_1 G'F'$,

or
$$M = \frac{(P/P_1)_t}{(P_1 P_1)_{\varDelta T}},$$

where the suffix indicates the instant at which $(P'P_1)$ is measured and all values refer to the curve AG'BGE and its asymptote XY. If the ball end were perfectly fixed M would have the value 2. Accordingly, assigning a coefficient unity to such an ideal case, the perfection of the reflexions in the experiments is measured by $M/2$, which is denoted by R in the table. The value of N increases uniformly with time, so that when N has been calculated for a time $2.l/U$ it only remains to determine N for times t and $\varDelta$T by simple proportion, and from the graph, N against α/α_1, to determine $P_1 P_1$ (as in Table XIII.) for these times.

R appears to vary fairly rapidly with the length of the bars and more slowly with the velocity of approach, but does not appear to depend on the radius of the ball end. The more rapid variation with the length is rather surprising, but as the results indicate some dependence of R on the maximum pressure during the contact (which is dependent on both v and l) the completeness of the reflexion must vary from instant to instant during any one collision, so that R is not a true coefficient in the ordinary sense and may well be affected by the amplitude of the returning wave. Thus, when the velocity of approach varies, for bars of a given length, although the maximum pressure between the surfaces varies, so also does the amplitude of the returning wave, and the slow variation of R with v may simply indicate a more complete reflexion of waves of small amplitude.

The interpretation of these impact phenomena in terms of a phase change and a coefficient of reflexion can only be regarded as a convenient means of summarizing the effects of the varying conditions of the reflexion during the process, and more detailed speculations on the factors affecting R would scarcely be justified without more direct experimental evidence.

TABLE XIV.

Radius of ball end 1·44 cm.

Length of bars (cm.).	Velocity (cm./sec.).	$(P/P_1)_{t'}$	$(P/P_1)_{\Delta T}$	R.
63·6	17·45	0·994	0·797	0·624
49·6	··	0·988	0·810	0·610
35·6	··	0·972	0·807	0·602
17·0	··	0·894	0·822	0·544
8·5	··	0·762	0·850	0·448
63·6	13·09	0·993	0·802	0·619
49·6	··	0·985	0·813	0·606
35·6	··	0·967	0·843	0·574
17·0	··	0·884	0·813	0·544
8·5	··	0·753	0·836	0·450·
63·6	8·73	0·989	0·817	0·605
49·6	··	0·979	0·821	0·596
35·6	··	0·953	0·825	0·578
17·0	··	0·864	0·831	0·520
8·5	··	0·733	0·814	0·450
63·6	4·36	0·979	0·796	0·615
49·6	··	0·967	0·810	0·597
35·6	··	0·930	0·803	0·578
17·0	··	0·832	0·803	0·518
8·5	··	0·695	0·802	0·433
63·6	2·18	0·968	0·826	0·586
49·6	··	0·949	0·822	0·577
35·6	··	0·912	0·823	0·544
17·0	··	0·787	0·784	0·502
8·5	··	0·642	0·774	0·415

TABLE XV.

Values of R.

Velocity of approach 17·45 cm./sec.

Length of bar (cm.).	63·6	49·6	35·6	17·0	8·5
Radius of ball end (cm.).	R.	R.	R.	R.	R.
4·60	0·600	0·606	0·585	0·547	0·492
0·98	0·636	0·602	0·595	0·557	0·488
0·159	0·647	0·567	0·552	0·462	0·372

After the most violent collision of the soft-ended bars flats of appreciable size (of the order of a millimetre in diameter) were formed on the ends of the bars, so that the circumstances correspond approximately to the collision of flat-ended bars except that the area of contact is not the full area of cross-section (fig. 8).
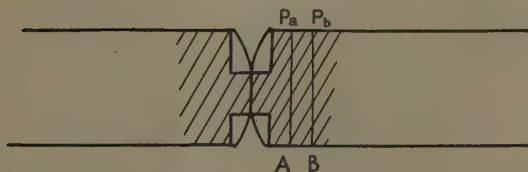
An approximate theory relating to impacts of this type may be formulated in the same manner as for hard-ended bars. Assume that the relation between the pressure and the indentation is now

$$P = k\alpha.$$

The equation of motion of a section AB near the ends in contact becomes

$$P_a - P_b + \frac{\ddot{\alpha}}{2}\rho U . dt = 0.$$

Fig. 8.

Integrating this, and substituting $\alpha = \alpha_1$ when $\dot{\alpha} = 0$,

$$k(\alpha_1 - \alpha) = \frac{\rho}{2} U\dot{\alpha},$$

which leads to

$$\frac{\rho U}{2} \log_e \left(\frac{1}{1 - \alpha/\alpha_1} \right) = kt$$

for the relation between α/α_1 and the time of growth of the wave. It will be seen that P/P_1, which is here equal to α/α_1, depends only on t and the shape and physical properties of the bars, not on the velocity of approach; the velocity affects only the scale of the pressure.

As before, when the pressure wave returns to the surface of contact it may be imperfectly reflected, but the conditions are simpler in that the area of contact will not

vary greatly during the process. The time of contact will again be given by an expression of the type

$$t = 2 \cdot l/U + \Delta T + \delta t,$$

where, as before, ΔT represents the time required for the wave to attain a fraction of its greatest pressure and δt represents a correction for phase changes. This correction was too small to be shown by the experimental results. If the coefficient of reflexion, R, were constant throughout, ΔT would be constant, so that t would be independent of v and would be a linear function of l over the whole range of the observations. Since the limiting pressure is proportional to v, the assumption that the area

Fig. 9.
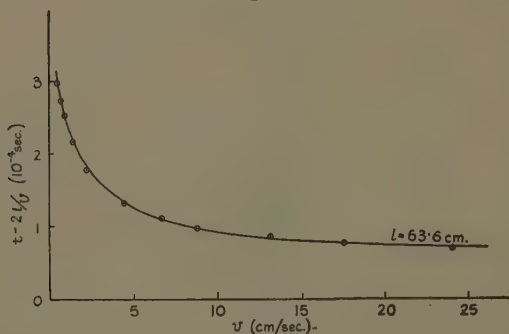
of contact does not vary is only an approximation. R may therefore be expected to vary somewhat with v, but as R can never exceed unity the least value of ΔT is the time required for the wave to grow to half its greatest pressure; this condition will be approached at the higher velocities. That this is in at least qualitative agreement with experiment is shown in fig. 9.

The flattening of the ends will have the effect of accelerating the growth of the pressure during contact, and it is probable that for lengths greater than about 30 cm. the pressure has practically attained its limiting value; if this is so, R should be independent of l for lengths greater than this, indicating a linear relation between t and l.

In conclusion, it is my pleasant duty to thank Professor J. E. P. Wagstaff (who suggested the problem) for his constant help and continued interest during the course of the investigation, and Mr. A. E. Beecroft, who prepared the bars used in the experiments.

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XVII. *The Application of the Heaviside-Bromwich Operational Method to the Solution of a Problem in Heat Conduction.* By ALEXIS LUIKOV *.

1. *Introduction.*

THE solution of problems of heat conduction and diffusion presents certain difficulties when the surface temperature varies with time, or radiation takes place into a medium of varying temperatures.

As a principle these problems may be solved by the classic Duhamel's method †. The defects of this method are as follows :—

(1) It requires the preliminary solution of a subsidiary problem with surface conditions, so that for the solution of the given problem a lot of time must be spent.

(2) The solution is obtained in form of several series, which are in need of an ulterior treatment.

To the solution of these problems there may be applied also the method of contour integrals developed by Carslaw ‡, and which possesses in comparison with

Duhamel's method a series of advantages : (1) it brings more quickly to definite results, and (2) gives a solution of a more simple aspect.   But this Carslaw's method is not, like that of Duhamel's, a general method for the solution of the given problems.   It requires an artificial composing of the solution in form of a contour integral for each separately considered concrete problem.   In the construction of the integrand, there must be a certain intuition in order that the composed function may give a solution corresponding to the problems set up.

The author of this paper has tried to apply the operational method of Heaviside, developed by Bromwich, to the solution of these problems.   As will be shown further on, the method under consideration leads also to some contour integral, *i. e.*, it possesses all the advantages of Carslaw's method, but compared with the latter it is a more general one, since the form of the integrand is obtained directly from the operational equation.

2. *Fundamental Notions.*

The following symbols are used :—

t = time

U = temperature.

U_m = temperature of the medium—

$$U_m = f(t).$$

λ = thermal conductivity.

$\kappa = \dfrac{\lambda}{c\rho}$ thermometric conductivity

c = specific heat.

ρ = density.

α = emissivity (surface conductivity).

The equation of heat conduction is

$$\frac{\partial U}{\partial t} = \kappa \nabla^2 U, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where ∇^2 is Laplace's operator.

The surface condition is
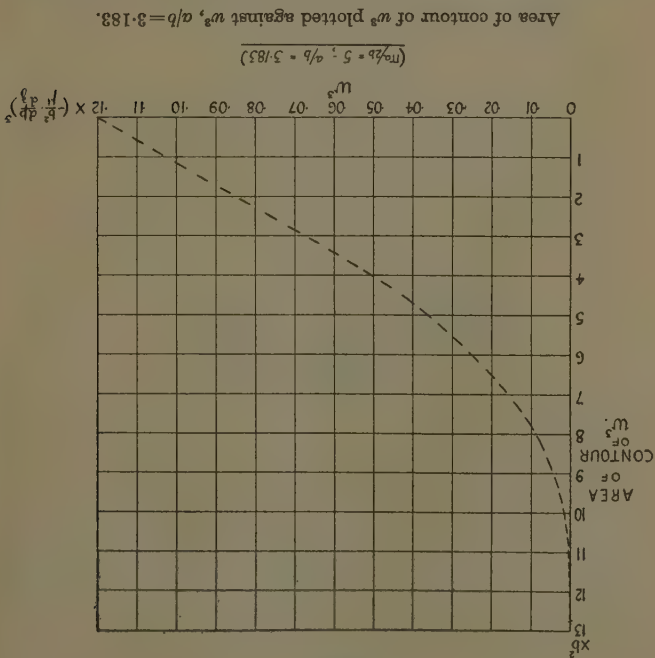
$$U = 0 \text{ initially (when } t = 0), \quad . \quad . \quad . \quad . \quad (2)$$

$$-\frac{\partial U}{\partial n} + H[f(t) - U] = 0 \text{ at the surface, } . \quad . \quad (3)$$
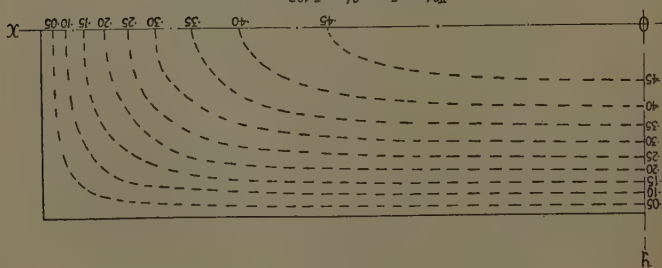
where $$H = \frac{\alpha}{\lambda}$$

Fig. 7.

$(m_{a/b} = 5 \; ; \; a/b = 3.183)$

Area of contour of w^3 plotted against w^3, $a/b = 3.183$.

It will be observed (fig. 3) that, when $a = b$, the area of the contour of w is almost a linear function of w; in streamline motion through a cylindrical pipe the relationship is *truly* linear.
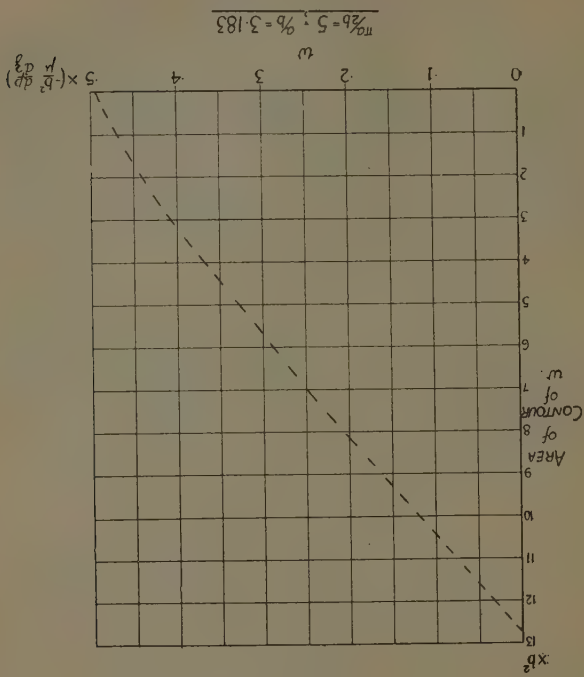
VI. *Summary.*

In the laminar motion of an incompressible viscous fluid through a pipe of rectangular cross-section the ratio of the true kinetic head to the apparent kinetic head based on the mean velocity in a cross-section is a function of the ratio of the width to the depth of the pipe. Fig. 1 gives this relationship. With a square section the ratio is 2·08 as compared with 54/35 or 1·5428 . . . for an infinitely wide passage.
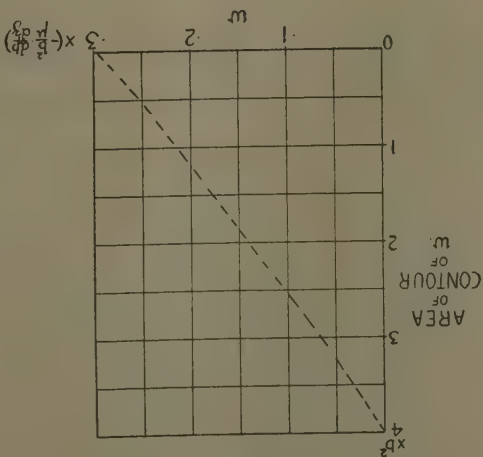
Section III.). It is reasonable to suppose that this part of this error will be eliminated in the final estimate of h_1/h_a, since both $\iint u^3\,wd\,x\,dy$ and $\iint u^3\,x\,p\,dy$ are determined graphically from the same original premises.

(b) The values have been checked independently by Mr. N. D. Grunberg, B.Sc., a research student working with the author in the Engineering Department of the Manchester University. Thus for a square section ($a=b$) he obtained $h_1/h_a=2.09$ (0), compared with 2.08 (0) by the author. His value of $\overline{w}$ was $-0.1397\,\dfrac{\mu}{b^2}\cdot\dfrac{l}{dp}\cdot\dfrac{dp}{dz}$, the average of this figure and the author's being thus $-0.1401\,\dfrac{\mu}{b^2}\cdot\dfrac{l}{dp}\cdot\dfrac{dp}{dz}$, compared with the calculated $-0.1406\,\dfrac{\mu}{b^2}\cdot\dfrac{l}{dp}\cdot\dfrac{dp}{dz}$, while the corresponding average of the two determinations of h_1/h_a is 2.085 as compared with the value of 2.08 (0) given in Section I.

Mr. Grunberg's determinations of h_1/h_a for $a/b=3.183$, 5, and 9.549 also agree with the author's within 0.4, 0.6, and 1.3 per cent. respectively.

V.

By way of illustration the following diagrams are submitted :—

Fig. 2.

$a = b.$
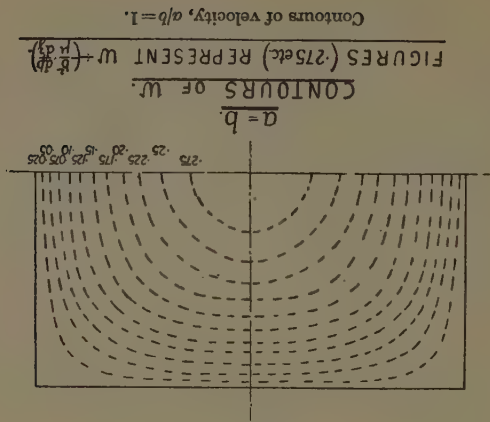
CONTOURS OF W.

FIGURES (·275etc.) REPRESENT $w \div \left(\dfrac{b^2}{\mu}\dfrac{dp}{dz}\right)$

Contours of velocity, $a/b=1.$

252   Mr. J. M. Allen *on the Kinetic Energy of*

to be drawn showing w in its relationship to y for various values of x.

(b) The family of curves referred to was utilized to plot contours of velocity in the cross-section.

(c) The areas embraced by these contours of velocity were measured by means of a planimeter.

(d) As a result of (c) it was readily practicable to plot a curve of (area of contour of velocity) against (velocity). Planimetry of this curve yielded the integral $\iint w\,dx\,dy$, and hence the mean velocity, $\overline{w}$.

(e) Also from (c) it was possible to plot a curve of (area of contour of w^3) against w^3, planimetry of which gave $\iint w^3\,dx\,dy$.

(f) From the results of (d) and (e) h_r and h_u were calculated with the aid of equations (1) and (2). Hence the ratio $h_r : h_u$ was derived.

III.

In order to check the accuracy of the graphical method, the value obtained for $\overline{m}$ by (d) of Section II. was compared with the calculated value of $\overline{m}$ given by equations (4) and (5). The comparison is stated below :—

Table II.

a/b.	$\overline{m} \div \left(-\dfrac{b^2}{h}\dfrac{dh}{dp} \right)$.		Ratio of graphical calculated values.
	From graphical method.	By direct calculation.	
Unity	0·1417	0·1406	1·008
3·183	·2662	·2674	0·9955
5	·2891	·2913	0·9925
9·549	·3104	·3114	0·9968

IV.

In Section I. it has been stated that the probable accuracy of the values quoted for h_r/h_u is ± 1 per cent.

This statement is a result of the following argument :—

(a) The maximum difference between the graphical and calculated values of $\overline{m}$ is less than 1 per cent. (see

the form of a curve drawn through the plotted points, and enables the true kinetic head to be speedily calculated for any rectangular pipe in which laminar flow is established. The curve closely resembles that obtained by plotting w_{max}/w against a/b[*].

II.

It is necessary to explain the method adopted for determination of the values already given.

The true kinetic head, h_{r}, is given by

$$h_{r} = \frac{1}{2g} \cdot \frac{\iint w^3 dx\, dy}{\iint w\, dx\, dy}, \quad \cdots \quad (1)$$

the integrals to be evaluated over the complete cross-section.

On the other hand, the apparent kinetic head, h_a, is given by

$$h_a = \frac{1}{2g}\, \overline{w}^2. \quad \cdots \quad \cdots \quad (2)$$

Now

$$w = -\frac{32\, r^2 b^2}{\pi^3} \left\{ \frac{\cosh(\pi x/2b)}{\cosh(\pi a/2b)} \cdot \cos\frac{\pi y}{2b} \right.$$

$$\left. -\frac{1}{3^3} \frac{\cosh(3\pi x/2b)}{\cosh(3\pi a/2b)} \cdot \cos\frac{3\pi y}{2b} + \cdots \right\} + r(b^2 - y^2),$$

$$\cdots \quad (3)$$

while

$$\overline{w} = \frac{Q}{4ab}, \quad \cdots \quad \cdots \quad \cdots \quad (4)$$

where

$$Q = -\frac{4}{3} \frac{ab^3}{\mu} \frac{dp}{dx} \left\{ 1 - \frac{192}{\pi^5} \cdot \frac{a}{b} \cdot \left(\tanh\frac{\pi a}{2b} \right. \right.$$

$$\left. \left. + \frac{1}{3^5} \tanh\frac{3\pi a}{2b} + \cdots \right) \right\} \quad \cdots \quad (5)$$

The integral $\iint w^3 dx\, dy$ assumes a most complicated form, and accordingly the following graphical method of evaluating h_r/h_a was employed :—
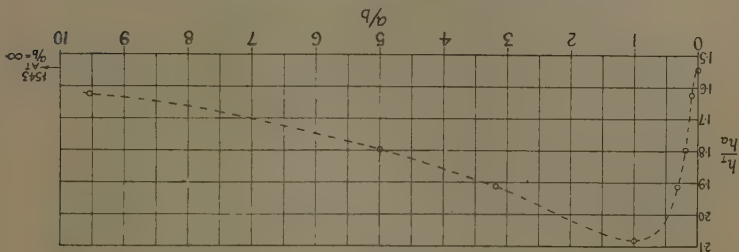
(*a*) Using equation (3), w was calculated for several values of x and y, thus enabling a family of curves

Similarly, for laminar motion in a very wide rectangular passage $(a:b) \to \infty$, the corresponding ratio may be readily found to $\to 54 : 35$, or $1 \cdot 5428 \ldots : 1$.

In conjunction with other values of $(a:b)$ different values will occur, and in particular when $a=b$ the ratio must be a maximum or a minimum, while it will be identical for $(a:b)=b/k$ and $(a:b)=1/k$.

The author has determined, by a process of graphical integration, the value of the ratio for $(a/b)=1$, $3 \cdot 183$, 5, and $9 \cdot 549$ respectively. The second and fourth of these values of (a/b) are equivalent to $(\pi a/2b)$ and 15 respectively, and the results obtained are set out in the following table :—

TABLE I.

$\pi a/2b$.	Ratio $a : b$.	Ratio of true kinetic head : apparent kinetic head.
	Unity	$2 \cdot 08(0)$
5	$3 \cdot 183$ (or $0 \cdot 3142$)	$1 \cdot 91(2)$
	5 (or $0 \cdot 2$)	$1 \cdot 79(6)$
15	$9 \cdot 549$ (or $0 \cdot 1047$)	$1 \cdot 62(3)$
	∞ (or zero)	$1 \cdot 643$

Fig. 1.

In the above table the value given for $(a:b)=\infty$ or zero is obtained by direct analysis; the remaining values, which are the result of graphical integration, are probably true within ∓ 1 per cent.

The accompanying diagram (fig. 1) shows the results in

XVIII. *The Kinetic Energy of Laminar Flow through Rectangular Passages.* By J. ALLEN, M.Sc., Assoc. M.Inst.C.E.*

List of Symbols.

a = half width of rectangular pipe.

b = half depth of rectangular pipe.

p = pressure.

Q = quantity flowing through pipe, per unit time.

w = velocity of a particle parallel to the axis of the pipe.

x = coordinate of particle, taking the centre of the section as origin and measuring parallel to the width.

y = coordinate, measuring parallel to the depth.

z = distance parallel to the longitudinal axis of the pipe.

μ = coefficient of viscosity.

$$\tau = -\frac{1}{2\mu} \cdot \frac{dp}{dz}.$$

g = acceleration due to gravity.

$\overline{w}$ = mean velocity in a cross-section.

h_T = true kinetic head.

h_a = apparent kinetic head.

I.

IN a previous paper †, the author has called attention to the fact that, in the laminar motion of an incompressible viscous fluid through a pipe of rectangular cross-section, (i.) the ratio of the maximum to the mean velocity in a given cross-section and (ii.) the position of the filament of mean velocity are functions of the ratio, $a : b$, of the width to the depth of the cross-section. It is a fact also that the ratio of the true to the apparent kinetic heads depends upon the ratio of width to depth, and the object of the present investigation was to derive a curve which would represent the general solution of (true kinetic head : apparent kinetic head) $= \phi(a : b)$.

In streamline motion along a pipe of circular cross-section it is easily shown that the true kinetic head is twice the apparent head calculated from the mean velocity.

From (19) it follows that

$$-A\sigma\,\text{sh}\,\sigma R + H_1(1 - A\,\text{ch}\,\sigma R) = 0, \quad \cdot\ \cdot\ \cdot \quad (20)$$

where

$$H_1 = \frac{\kappa}{\alpha_1}$$

and, therefore,

$$A = \frac{H_1}{H_1\,\text{ch}\,\sigma R + \alpha\,\text{sh}\,\sigma R},$$

$$\frac{\Omega}{\Omega_0} = 1 - \left\{ \frac{\text{ch}\left[\left(q^2 + \frac{\kappa}{\lambda}\right)^{\frac14} x\right]}{\left(q^2 + \frac{\kappa}{\lambda}\right)^{\frac14}\text{ch}\left[\left(q^2 + \frac{\kappa}{\lambda}\right)^{\frac14} R\right] + \frac{H_1}{\left(q^2 + \frac{\kappa}{\lambda}\right)^{\frac14}}\cdot\text{sh}\left[\left(q^2 + \frac{\kappa}{\lambda}\right)^{\frac14} R\right]} \right\} \quad \cdot\ \cdot\ \cdot \quad (21)$$

Bromwich's rule gives

$$\frac{\Omega}{\Omega_0} = 1 - \frac{1}{2\pi i}$$

$$\times \int \frac{\text{ch}\left[(z+H_2^2 R_2^2)^{\frac14}\,\frac{x}{R}\right]}{\text{ch}\,(z+H_2^2 R_2^2)^{\frac14} + \frac{1}{H_1 R}(z+H_2^2 R_2^2)^{\frac14}\cdot\text{sh}\,(z+H_2^2 R_2^2)^{\frac14}}$$

$$\times e^{\frac{\kappa z t}{R^2}}\cdot\frac{dz}{z}, \quad \cdot\ \cdot\ \cdot \quad (22)$$

where

$$H_2 = \frac{\kappa}{\beta}.$$

The solution given in (22) reduces to

$$\frac{\Omega}{\Omega_0} = 1 - \frac{\text{ch}\,H_2 x}{\text{ch}\,H_2 R + \left(\frac{H_2}{H_1}\right)\text{sh}\,H_2 R}$$

$$+ \sum_{n=1}^{\infty}\mu_n^2\cdot\frac{2\sin\mu_n\cos\mu_n\frac{x}{R}}{(\mu_n^2+H_2^2 R_2^2)(\mu_n+\sin\mu_n\cos\mu_n)}\cdot e^{-\left(\frac{\kappa\mu_n^2}{R_2}+s\right)t},$$

where μ_n is the nth positive root of the transcendental trigonometric equation

$$\cot\mu_n = \frac{\mu_n}{H_1 R}. \quad \cdot\ \cdot\ \cdot \quad (23)$$

Thus we have the mean temperature

$$\bar{U} = \frac{1}{R}\int_0^R U\,dx = 1 - \frac{tg\ HR}{HR}\,e^{-\alpha t}$$

$$+ \sum_{n=1}^{\infty}\frac{2H^2R^2}{\mu_n^2(\mu_n^2-H^2R^2-HR^2)}\cdot e^{-\frac{g\mu_n^2}{R^2}t} \quad \cdot \quad (13.4)$$

In the theory of the conduction of heat there is a series of problems which, at their solution by means of Duhamel's method, lead to problems with variable surface conditions.

By applying the operational method these problems can be solved in a very simple way.

5. *Finite Rod; reaction at ends into a medium at zero temperature. Initial temperature* U_0=const. *Radiation at the surface.*

When the surface is not impervious to heat and the temperature of the medium is taken as zero, the equation for the temperature is

$$\frac{\partial U}{\partial t} = \kappa\frac{\partial^2 U}{\partial x^2} - \beta U, \quad \cdot \quad \cdot \quad \cdot \quad (18)$$

where

$$B = \frac{\alpha_2 p}{c\rho\omega} = \text{const.}$$

p=perimeter of the cross-section of the rod,

ω=area of the cross-section.

α_2=emissivity.

The surface condition is then

$$\frac{\partial U}{\partial x} + \frac{\alpha_1}{\lambda}U = 0, \quad \text{at} \quad x = \pm R, \quad \cdot \quad \cdot \quad (19)$$

where $\alpha_1 \neq \alpha_2$; $U = U_0$ at $t=0$.

Let us put

$$\sigma^2 = q^2 + \frac{\beta}{\kappa}$$

and write the equation

$$\frac{\partial^2 U}{\partial x^2} - \sigma^2(U - U_0) = 0.$$

The solution is

$$\frac{U}{U_0} = 1 - A\ ch\ \sigma x.$$

If we take

$$e^{-ct} = U_o - U \mp R \qquad at \ x = \pm R \quad \cdots \quad (14)$$

we have

$$-c e^{-ct} = -\kappa q^2 U_o. \qquad \cdots \quad (15)$$

From (14) and (15) it follows that

$$U = \frac{cU_o}{c + \kappa q^2} \quad at \ x = \pm R. \quad \cdots \quad (12)$$

Hence, using the surface conditions (12.1), we find

$$\frac{U_o}{1 + \frac{\kappa}{c} q^2} = A \operatorname{ch} qR; \quad A = \frac{U_o}{\left(1 + \frac{\kappa}{c} q^2\right) \operatorname{ch} qR} \quad \cdots \quad (16)$$

Substituting the expression for A in solution (13), we have

$$\frac{U}{U_o} = \frac{\operatorname{ch} qx}{\left(1 + \frac{\kappa}{c} q^2\right) \operatorname{ch} qR} \quad \cdots \cdots \quad (13.1)$$

Applying the above rule, due to Bromwich, we find

$$\frac{U}{U_o} = \frac{1}{2\pi i} \int_L \frac{\operatorname{ch} z^{\frac{1}{2}} \frac{x}{R}}{\left(1 + \frac{HR^2}{z}\right) \operatorname{ch} z^{\frac{1}{2}}} \cdot e^{\frac{\kappa z t}{R^2}} \cdot \frac{dz}{z} \quad \cdots \quad (13.2)$$

where $\qquad H = \sqrt{\frac{c}{\kappa}}.$

The integrand on the right-hand side of the formula (13.2) is a single-valued function of z with poles at

(1) $z = 0$,

(2) $z = -H^2 R^2$,

(3) $z = -\mu_n^2$,

where $\qquad \mu_n = \frac{(2n-1)\pi}{2}$; $\quad n = 1, 2, 3 \ldots$ etc.

Hence, using the principle of residues, we easily find

$$\frac{U}{U_o} = 1 - \frac{\cos H x}{\cos H R} e^{-ct} + \sum_{n=1}^{\infty} (-1)^{n+1} \frac{2 H^2 R^2 \cos \mu_n \frac{x}{R}}{\mu_n(\mu_n^2 - H^2 R^2)} \cdot e^{-\frac{\kappa \mu_n^2 t}{R^2}}. \quad \cdots \quad (13.3)$$

If we put $\alpha \to \infty$ (HR$\to\infty$), then the surface condition becomes

$$U = \theta \, . \, t \quad \text{at} \quad r = R.$$

Substituting in (7) HR $= \infty$ we have

$$\frac{U}{\theta} = t - \frac{R^2 - r^2}{6\kappa} + \frac{2R^2}{\kappa} \sum_{n=1}^{\infty} (-1)^{n+1} \frac{1}{\mu_n^3} \frac{R}{r} \sin \mu_n \frac{r}{R} \cdot e^{-\frac{\kappa \mu_n^2 t}{R^2}}, \qquad (8)$$

where

$$\mu_n = n\pi, \quad n = 1, 2, 3 \ldots \text{etc.} \qquad \cdots$$

The mean temperature is given by

$$\underline{U} = \frac{3}{R^3} \int_0^R r^2 U \, dr,$$

$$\underline{U} = \theta t - \frac{\theta R^2}{15\kappa} + \frac{6\theta R^2}{\kappa \pi^4} \sum_{n=1}^{\infty} \frac{1}{n^4} e^{-\frac{\kappa n^2 \pi^2 t}{R^2}}. \qquad (9)$$

and this result agrees with that calculated by T. J. I'a. Bromwich *.

4. *The Surface of a Plane Slab is maintained at Temperature* $U = U_c (1 - e^{-\omega t})$.

The differential equation for U in the infinite slab can be written

$$\frac{\partial U}{\partial t} = \kappa \frac{\partial^2 U}{\partial x^2}, \qquad \cdots \quad (10)$$

$$U = 0 \quad \text{when} \quad t = 0. \qquad \cdots \quad (11)$$

$$\left.\begin{array}{l} (a) \ \text{Symmetry with respect to } x\,; \\ (b) \ U = U_c(1 - e^{-\omega t}) \ \text{at } x = \pm R, \end{array}\right\} \quad (12)$$

where 2R is the thickness of the slab and c is a constant.

Equation (10) may be written

$$\frac{q^2 U}{\kappa} = \frac{\partial^2 U}{\partial x^2}.$$

Solving this as an ordinary differential equation, and choosing, in accordance with condition (12 a), the solution symmetrical in x, we have

$$U = A \, \mathrm{ch} \, qx, \qquad \cdots \quad (13)$$

where A is independent of x.

* Bromwich, Phil. Mag., xxxvii. p. 134 (1919).

Provided m be a fractional number, then the integrand will be a many-valued function, and with $z = 0$ we shall have the critical point (point de ramification, verzweigungspunkt or punto die diramazione or punto di giramiunto).

If we put $m = 1$, then the surface condition becomes

$$- \frac{\partial \varrho}{\partial r} + H(\theta - U) = 0 \text{ at } r = R.$$

Hence the solution (6) can be written

$$\frac{\theta}{U} = \int_L \frac{r}{R} \frac{\text{sh} \, z^{\frac{1}{2}}}{HR^{\frac{1}{4}} \left(HR - 1 \right) \text{sh} \, z^{\frac{1}{2}} + z^{\frac{1}{2}} \text{ch} \, z^{\frac{1}{2}}} \cdot e^{\frac{kzt}{R^2}} \frac{dz}{z^2} \quad . \quad (6.1)$$

The formula (6.1) gives the complete solution of the differential equation in terms of contour integrals. The integrand on the right-hand side of the formula (6.1) is a single-valued function of z with poles at

$$(1) \quad z = 0,$$

$$(2) \quad z = -\mu_n^2,$$

where $n = 1, 2, 3 \ldots$ etc.

μ_n is the nth positive root of the transcendental trigonometric equation

$$(HR - 1) \sin \mu_n + \mu_n \cos \mu_n = 0.$$

Hence, using the principle of residues, we easily find

$$E_1 = + t + \frac{6k}{r^2 - R^2 \left(1 - \dfrac{2}{HR} \right)}$$

$$E_2 = - \frac{2HR^4}{r} \frac{\sin \mu_n \frac{r}{R}}{R} \sum_{n=1}^{\infty} \frac{\mu_n^3 (HR \cos \mu_n - \mu_n \sin \mu_n)}{kr} \cdot e^{-\frac{k\mu_n^2 t}{R^2}}$$

and, therefore,

$$\frac{\theta}{U} = 2\pi i \Sigma \text{ res. },$$

$$\frac{\theta}{U} = t - \frac{6k}{R^2 \left(1 + \dfrac{2}{HR} \right) - r^2}$$

$$+ \frac{2R^3}{r} \frac{\sin \mu_n \frac{r}{R}}{R} \sum_{n=1}^{\infty} HR \frac{\mu_n \sin \mu_n - HR \cos \mu_n}{\mu_n^3} \cdot e^{-\frac{k\mu_n^2 t}{R^2}} \right\} \quad . \quad (7)$$

The solution is

$$\Omega = \frac{A}{r} \operatorname{sh} qr, \qquad \cdot \quad \cdot \quad \cdot \quad (4.1)$$

where A is independent of r but involves q. We can write
the surface condition (3.4) in the form

$$\theta t^n = \frac{1}{H} \frac{\partial \Omega}{\partial r} + \Omega \quad \text{at} \quad r = R. \quad \cdot \quad \cdot \quad (3.5)$$

We have

$$\frac{m}{p} \theta t^{n-1} = \kappa q^2 \left[\frac{1}{H} \frac{\partial \Omega}{\partial r} + \Omega \right] \cdot \cdot (3.6)$$

From (3.5) and (3.6) it follows that

$$\frac{\partial \Omega}{\partial r} + H \left[\Omega - \left(\frac{m}{\kappa q^2} \right) \theta \right] = 0 \quad \text{at} \quad r = R. \quad (3.7)$$

Hence, using the surface condition (3.7), we find

$$-\frac{Aq}{R} \operatorname{ch} qR + \frac{A}{R^2} \operatorname{sh} qR + H \left[\theta \left(\frac{m}{\kappa q^2} \right) - \frac{A}{R} \operatorname{sh} qR \right] = 0,$$

$$A = \frac{H\theta \left(\frac{m}{\kappa q^2} \right) \cdot R^2}{(HR - 1) \operatorname{sh} qR + qR \operatorname{ch} qR}.$$

Substituting this in solution (4.1), we arrive at the opera-
tional solution

$$\frac{\Omega}{\theta} = \frac{HR^2}{r} \left(\frac{m}{\kappa q^2} \right) \frac{\operatorname{sh} qr}{(HR - 1) \operatorname{sh} qR + qR \operatorname{ch} qR}. \quad \cdot \quad (5)$$

Applying the above rule, due to Bromwich, we find

$$\frac{\Omega}{\theta} = \frac{1}{2\pi i} \int_L HR^2 \left(\frac{m}{\kappa R^2} \right)_m \frac{\operatorname{sh} z^{\frac{1}{2}} \frac{R}{r}}{(HR - 1) \operatorname{sh} z^{\frac{1}{2}} + z^{\frac{1}{2}} \operatorname{ch} z^{\frac{1}{2}}}$$

$$\times e \frac{R^2}{R^2} \cdot \frac{dz}{z^{m+1}}, \quad \cdot \quad \cdot \quad (6)$$

where

$$z = \frac{\nu R^2}{\kappa}.$$

The value of z is always positive or zero, and the remaining
term in the integrand approaches zero uniformly with
respect to arg z as $|z| \to \infty$, with a possible exception
when

$$-\pi + \epsilon \leqslant \operatorname{arg} z \leqslant \pi - \epsilon,$$

where ϵ is arbitrarily small. Hence the integral along L
is equivalent to the integral around a large circle.

R 2

Let us make use of the rule, due to Bromwich, which states that provided $\phi(p)$ is an analytic function of v then

$$\phi(p) = \frac{1}{2\pi i}\int_{L} e^{vq}\phi(v)\,\frac{dv}{v}$$

where L is a curve in the v-plane and extends from $a-1\infty$ to $a+i\infty$ (where a is positive and finite), and is such that all the singularities of the integrand are on the $-\infty$ side of the path.

Recalling that $g = \dfrac{p^{\frac{1}{2}}}{\kappa^{\frac{1}{2}}}$, and applying the above-mentioned rule, we find

$$U = \frac{1}{2\pi i}\int_{L} \phi(x,y,z,\xi)e^{\xi\kappa^{\frac{1}{2}}}\,\frac{d\xi}{\xi}, \quad \cdots \quad (5)$$

where

$$\xi = \frac{v}{\kappa}.$$

The function $\phi(x, y, z, \xi)$ results from the function $f(x, y, z, q)$ by substituting ξ for κq^2.

For positive values of t, v may usually be taken to be any curve beginning at infinity in the third quadrant, passing round the origin and proceeding to infinity again in the second quadrant, provided that all the singularities of the integrand remain on the same side of the curve as $-\infty$.

Let us see by a series of examples in which way the function $\phi(\xi, x, y, z)$ can be found.

For the sake of simplicity of the exposition let us consider this method in its application to one-dimension problems of heat conduction.

3. *Conduction of Heat in a Sphere with Radiation at the Surface.*

The differential equation for U in the sphere can be written

$$\frac{\partial(rU)}{\partial t} = \kappa\frac{\partial^2}{\partial r^2}(rU), \quad \cdots \quad (1.2)$$

$$U = 0 \quad \text{when } t = 0, \quad \cdots \quad (2.2)$$

$$-\frac{\partial U}{\partial r} + H(\theta_m - U) = 0 \text{ at } r = R. \quad \cdots \quad (3.4)$$

The equation (1.1) may be written

$$\frac{\partial^2}{\partial r^2}(rU) = g^2(rU). \quad \cdots \quad (1.3)$$

Now writing symbolically p for $\dfrac{\partial}{\partial t}$, we get

$$\kappa^2 = p = \frac{\partial}{\partial t},$$

where p is Heaviside's operator.

Hence the equation of heat conduction is

$$\triangle^2 U = q \, U. \qquad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (1.1)$$

We find the solution of the equation (1.1) in the form

$$U = f(x, y, z, q). \qquad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (4)$$

The operational solution (4) is then the function of q and x, y, z.

The aspect of the function itself is determined by the geometrical form of the body and its constant coefficients—from the satisfaction of the surface conditions.

By changing the surface condition (3) in such a way as to be able to represent the function $f(t)$ in the form of the function of the operator q, we have

$$
\left\{
\begin{aligned}
f(t) &= \frac{1}{\varrho}\frac{\mathrm{H}}{\partial n} U + U, \\[2mm]
f'(t) &= \frac{d}{dt}\left[\frac{1}{\varrho}\frac{\mathrm{H}}{\partial n} U + U\right].
\end{aligned}
\right.
\qquad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (3.1)
$$

Substituting the operator κ^2 for $\dfrac{d}{dt}$, we get

$$f(t) = \kappa^2 \left[\frac{1}{\varrho}\frac{\mathrm{H}}{\partial n} U + U\right] \quad \cdot \quad \cdot \quad \cdot \quad (3.2)$$

Excluding from the formulæ (3.1) and (3.2) we get the possibility of writing the surface condition in the form

$$\frac{1}{\varrho}\frac{\mathrm{H}}{\partial n} U + U = \psi(\kappa q^2) \text{ at the surface.} \quad \cdot \quad \cdot \quad (3.3)$$

Provided the function $U_m = f(t)$ is given, its aspect $\psi(\kappa q^2)$ will be determined by means of the solution of the system of equations (3.1) and (3.2).

If the solution (4) satisfies the surface condition (3.3) we get

$$U = f_1(x, y, z, q),$$

where the function $f_1(x, y, z, q)$ will depend only upon the geometrical form of the body.

XIX. *The Determination of the Coefficient of Accommodation from Aspects of the Temperature Drop Effect. By* H. SPENCER GREGORY, *Ph.D., A.R.C.S., D.I.C., Imperial College* *.

I N recent years calculations of the coefficient of thermal accommodation have been made in terms of the temperature discontinuity existing between a heated solid surface and the adjacent gas. Such temperature drop has been found to depend on the nature and pressure of the gas, and the experimental data on which these calculations are based is expressible in terms of the heat transfer at relatively low gas pressure, or on the more recently developed investigations associated with the heat losses from an electrically heated wire disposed in gases at much higher pressures. These latter investigations are complicated to some extent by the existence of convection, in which heat is carried away from the wire by mass motions of the gas itself. Such losses can be obviated by careful consideration of the dimensions of the enclosing vessel in which the wires are mounted, and by lowering the gas pressure. Although such procedure causes the troublesome temperature drop effect to be enhanced, the theoretical and experimental aspects of the problem have now been brought to a successful issue.

For a given difference of temperature between the wire and enclosing vessel the heat transfer at low pressure is markedly less than over the pressure range in which the heat transfer is independent of pressure, apart from the region adjacent to the wire.

At the same time the corresponding periods of time required for attainment of the stationary state is very much greater in the case when the gas is rarefied. As against this the temperature drop effect is greater at lower pressure, and for this reason the investigations at low pressure possess advantages in comparison with those investigations in which heat conduction is of first importance and in which the time factor is less laborious in practice.

The temperature discontinuity [1] existing at the

* Communicated by the Author.

surface of separation between a heated solid and a gas is defined by the relation

$$\delta\theta = -\mu d\theta/dn, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which $d\theta/dn$ represents the temperature gradient at a point in the gas near to the surface in a normal direction, and μ a quantity found to be proportional to the mean free path λ of the gas molecules.

The quantity μ [2] was calculated by Smoluchowski in terms of the assumption that molecules can be regarded as centres of forces of repulsion varying inversely as the fifth power of the distance of separation. In this way $\delta\theta$ is expressible in the form

$$\delta\theta = \frac{15}{2\pi} \cdot \frac{2-\alpha}{2\alpha} \cdot \lambda \cdot \frac{d\theta}{dn}, \quad . \quad . \quad . \quad . \quad (2)$$

where α is the accommodation coefficient as defined by Knudsen and λ the mean free path.

According to Knudsen [3] α is defined in terms of the mean energies of the molecules approaching and rebounding from the heated solid surface. If T_1 represents the temperature (abs.) of the heated surface, and T_1', T_1'' the average temperature of the molecules rebounding from and approaching the surface of the wire, and if E_1, E_1', E_1'' represent the average energies of the molecules corresponding to these temperatures, then, from Knudsen,

$$\alpha = \frac{E_1' - E_1''}{E_1 - E_1''} = \frac{T_1' - T_1''}{T_1 - T_1''}, \quad . \quad . \quad . \quad (3)$$

providing also that the velocity distribution of the molecules rebounding from the heated surface corresponds to a Maxwellian distribution.

In the absence of convection the equation expressing thermal equilibrium between a uniformly heated wire and a concentrically disposed cylindrical surface is represented by

$$Q \log \frac{r_2 - \lambda_2}{r_1 + \lambda_1} = 2 \cdot \pi \cdot k \cdot l \cdot (T_1 - T_2 - \delta\theta_1 - \delta\theta_2), \quad . \quad (4)$$

where T_1 and T_2 are the temperatures of the wire and wall, $\delta\theta_1$ and $\delta\theta_2$ the temperature drops at the surfaces of the wire and wall respectively, λ_1 and λ_2 the mean free paths of the gas molecules corresponding to a pressure p and at temperatures T_1 and T_2, r_1 and r_2 the radii of the

wire and internal surface of the tube, while k is the absolute conductivity of the gas at the mean temperature of the gas layer ; Q is the heat transfer per second corrected for radiation from a wire of length l whose temperature is regarded as being constant throughout its length.

From (2) we have

$$\delta\theta_1 = \frac{15}{2\pi} \cdot \frac{2-\alpha}{2\alpha} \cdot \lambda_1 \cdot \frac{Q}{2 \cdot \pi \cdot k_1 \cdot l \cdot r_1} , \quad . \quad . \quad (5)$$

$$\delta\theta_2 = \frac{15}{2\pi} \frac{2-\alpha'}{2\alpha'} \lambda_2 \cdot \frac{Q}{2 \cdot \pi \cdot k_2 \cdot l \cdot r_2} \quad . \quad . \quad . \quad (6)$$

Substituting (5) and (6) in (4),

$$Q \cdot \log_e \frac{r_2 - \lambda_2}{r_1 + \lambda_1} = 2 \cdot \pi \cdot k \cdot l \cdot (T_1 - T_2)$$
$$- \frac{15}{2\pi} Q \cdot k \cdot \left(\frac{2-\alpha}{k_1 r_1 2 \cdot \alpha} \lambda_1 + \lambda_2 \frac{2-\alpha'}{k \ r_2 2 \cdot \alpha'} \right), \quad (7)$$

where k_1 and k_2 are the thermal conductivities of the gas at the temperatures T_1 and T_2.

In relation to actual practice it is possible to modify equation (7). If r_2/r_1 is of the order of about 250/1 it is sufficiently accurate to write $\alpha' = \alpha$ and $k_2 = k_1$.

For values of r_1 not less than 4 mils, and restricting the pressure range in actual experiments so that λ_1 and λ_2 are of negligible magnitude in comparison with r_1 and r_2, we have the simplified equation

$$\frac{1}{Q} = \frac{\log r_2/r_1}{2\pi k \cdot l \cdot \theta} + \frac{A}{2 \cdot \pi \cdot k_1 \cdot l \cdot \theta p} , \quad . \quad . \quad (8)$$

where $\quad A = \frac{15}{2\pi} \cdot \lambda_0 \cdot p_0 \cdot \left(\frac{2-\alpha}{2 \cdot \alpha} \right) (1/r_1 + 1/r_2),$

and, further, $\quad \lambda_2 = \lambda_1 = \lambda_0 \cdot p_0 ./p,$

λ_0 being the mean free path at a pressure of one atmosphere p_0.

In the absence of convection a linear relation should hold between $1/Q$ and $1/p$, from which k and α can be determined.

Equation (8) [4] was first applied to a re-examination of the results contained in the original experiments of Gregory and Archer [5] on the heat conduction through air and hydrogen. In this instance the correction for the

temperature drop effect was found to be of little con-
sequence, owing to the relatively large diameters (6 mils)
of the wires employed, and the equation was afterwards
more rigidly tested by Dr. Dickens [6] in relation to his
more recent work on gases varying widely in molecular
weight, and found to give very satisfactory results for
the thermal conductivity.

More careful consideration must be given to equation (7)
in the case where the diameter of the central wire is
less than 4 mils, and more especially in relation to investi-
gations at high temperature, in which the mean free path
becomes comparable with the radius of the wire ; the
reduction of pressure in order to obviate the convective
losses is also of serious aspect in regard to the free path.

The author [7], in his experiments on the effect of
temperature on the heat conduction through H_2 between
0° and 330° deg. Cent., used a modification of equation (7)
given by

$$\frac{Q}{\theta} \log \frac{r_2 - \lambda_2}{r_1 + \lambda_2} = 2 \cdot \pi \cdot k \cdot l.$$
$$- \frac{15}{2\pi} \frac{\lambda_0 p_0}{p} \frac{2-\alpha}{2 \cdot \alpha} \frac{1}{\log r_2/r_1} \frac{k}{k_1} (1/r_1 + 1/r_2). \quad (9)$$

This was arrived at by putting

$$Q = \frac{2 \cdot \pi \cdot k \cdot l \cdot \theta}{\log r_2/r_1}$$

in the small term on the right-hand side of equation (7).
The equation was also tested by Mr. C. T. Archer [8]
in relation to similar investigations on CO_2 over the
same range of temperature.

The Smoluchowski relation, which has been used by
the author and others to calculate the accommodation
coefficient from data in which the thermal conductivity
was of primary importance, is based on assumptions
which are strictly applicable to monatomic gases only,
and for this reason the author has been led to develop
a more general form of the modified Fourier equation,
from which the accommodation coefficient can be found
in terms of the known experimental values of the specific
heats of gases, and which does not depend on a numerical
factor applicable only to gases in the monatomic state.

In the figure, which represents the cross-section of a wire
coaxial with a tube, if T_1'' denotes the mean temperature

of the gas distant one mean free path from the surface of the wire, T_1 the temperature of the wire, and T_1' the mean temperature of the molecules rebounding from the wire, then, from Knudsen, the temperature drop at the metal gas interface is given by

$$\delta\theta_1 = T_1 - 1/2 . (T_1' + T_1'').$$

Since also
$$\alpha = \frac{(T_1' - T_1'')}{(T_1 - T_1'')},$$

therefore
$$\delta\theta_1 = \frac{(2-\alpha)}{2}(T_1 - T_1'');$$

hence
$$\delta\theta_1 \frac{2.\alpha}{(2-\alpha)} = (T_1' - T_1''). \quad . \quad . \quad . \quad . \quad (10)$$
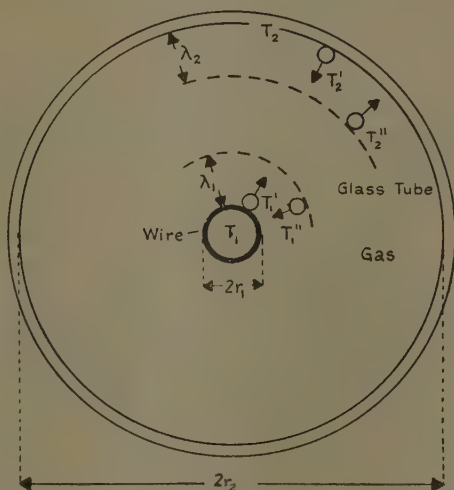
For a state of thermal equilibrium the gas molecules striking the filament come from a region distant λ_1 from the surface of the wire, the mean temperature of the molecules being T_1''; the number of such molecules crossing the area $2\pi . (r_1 + \lambda_1) . l$ per second is given by

$$N_1 = 2\pi . (r_1 + \lambda_1) l . n . C_1'' / \sqrt{6\pi},$$

where l is the length of the filament of uniform temperature T_1 and n, C_1'', the molecular concentration and root mean square velocity at T_1''.

Of this number a fraction $r_1/(r_1+\lambda_1)$ will collide with the filament; hence the number colliding or rebounding from the filament per second

$$=2.\pi.r_1.l.n.C_1''/\sqrt{6.\pi}.$$

The average internal energy possessed by each incident molecule is $(\beta-3/2).K.T_1''$, where $\beta.K$ is the specific heat at constant volume per molecule in ergs per deg. abs. temp. and K the Boltzmann constant per molecule $(1\cdot371.10^{-16}$ ergs per deg.).

Since we are concerned in the present case with the average energy of molecules rebounding from a surface, and since also in this case the average translational energy is $2.K.T_1''$ and not $3.K.T_1''/2$, we have for the average total energy associated with the emitted molecule an amount

$$(\beta-\tfrac{3}{2}).K.T_1''+2.K.T_1''$$
$$=(\beta+1/2)K.T_1'' \text{ per molecule.}$$

If the rebounding molecules possess an average temperature T_1', then the rate at which energy is transmitted from the filament

$$Q=2\pi.r_1.l.n.C_1''.K.[(\beta+1/2)T_1'-(\beta'+1/2)T_1'']/\sqrt{6\pi},$$
$$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad . \quad . \quad . \quad . \quad (11)$$

in which a possible variation of β with 'temperature from T_1' to T_1'' is allowed for.

Since $n=p/K.T_1''$, and $C_1''=\sqrt{3.R.T_1''}/M$, where R is the gas constant per gram molecule and M the molecular weight, we have, from (3), (10), and (11),

$$Q=2.\pi.r_1.l.\sqrt{R/2.\pi.M.T_1''}.\left[T_1(\beta-\beta')\right.$$

$$\left.+\{(\beta+1/2).\alpha-(\beta-\beta')\}\frac{2.\delta\theta_1}{2-\alpha}\right]. \quad (12)$$

In actual practice β varies only slowly with temperature, and the change of β is negligible over the range T_1' to T_1''; hence it is sufficiently accurate to write $\beta=\beta'$ in (12), and solving for $\delta\theta_1$ we obtain

$$\delta\theta_1=\frac{Q.\sqrt{2.\pi.M}.\sqrt{T_1''}.(2-\alpha)}{\sqrt{R}.2.\pi.r_1.l.2.\alpha(\beta+1/2).p} \quad . \quad . \quad (13)$$

Equation (13) represents the general expression for the temperature drop from which the Smoluchowski

relation can be deduced as follows : if k'' denotes the thermal conductivity of the gas at T_1'', then from (13)

$$\delta\theta_1 = \frac{(2-\alpha)}{2.\alpha} \frac{Q.k''}{2.\pi.l.r_1k''} \frac{\sqrt{2.\pi.M.T_1''}}{\sqrt{R}\,p(\beta+1/2)}$$

$$= \frac{(2-\alpha)}{2.\alpha}\left(\frac{d\theta}{dr}\right)_{r_1} . \frac{f.\eta''C_v''}{p(\beta+1/2)} \frac{\sqrt{2.\pi.M.T_1''}}{\sqrt{R}}, \quad . \quad . \quad (14)$$

where η'' and C_v'' are the viscosity and specific heat at constant volume per gram of the gas at a temperature T_1'', f is a factor depending on the force operating in molecular collision.

For gases in the monatomic state,

$$C_v'' = 3.R/2.M,$$

$$\eta'' = \rho''v''.\lambda_1/\pi,$$

$$v'' = \frac{\sqrt{8.R.T_1''}}{\sqrt{\pi.M.}},$$

$$f = 2.5 \text{ (Chapman)},$$

where ρ'' is the density of the gas and v'' the arith. mean velocity ; hence from (14)

$$\delta\theta_1 = \frac{(2-\alpha)}{2.\alpha}\left(\frac{d\theta}{dr}\right)_{r_1} \frac{4.\lambda_1 f.\beta}{\pi(\beta+1/2)}$$

$$= \frac{(2-\alpha)\lambda_1}{2.\alpha} \frac{15}{2.\pi}\left(\frac{d\theta}{dr}\right)_{r_1},$$

which is in agreement with the Smoluchowski calculation for monatomic gases.

In the following table calculated values of the factor

Gas.	$f.$	$\beta.$	$\dfrac{4f.\beta}{\pi.(\beta+1/2)}.$
He ⎫ A ⎬ ...... Ne ⎭	2·5	3/2	$\dfrac{15}{2\pi}=2\cdot38$
CO	1·92	2·51	2·04
H_2	1·94	2·43	2·05
N_2	1·98	2·47	2·10
O_2	1·98	2·52	2·11
CO_2	1·64	3·38	1·82
NO_2.........	1·71	3·41	1·90
SO_2	1·47	3·75	1·65
NH_3.........	1·44	3·85	1·60
Air	1·97	2·48	2·09

$4 \cdot f \cdot \beta/\pi \cdot (\beta+1/2)$, in terms of the experimental data for f and β, are tabulated for several polyatomic gases.

The most serious divergence of the factor

$$4 \cdot f \cdot \beta/\pi \cdot (\beta+1/2)$$

from the Smoluchowski value for monatomic gases is that associated with NH_3, to an amount of about 30 per cent., and a corresponding error will exist in calculations of the accommodation coefficient for polyatomic gases from considerations of the Smoluchowski relation. The factor $4 \cdot f \cdot \beta/\pi \cdot (\beta+1/2)$, from its dependence on the quantity β, will therefore for polyatomic gases be a function of the temperature.

The application of the general temperature drop relation, as deduced above, to the determination of both the thermal conductivity and the accommodation coefficient is similar in procedure to that outlined above in regard to the Smoluchowski relation.

Writing (13) in the form

$$\delta\theta_1 = \frac{Q \cdot \sqrt{T_1}''}{p \cdot r_1 \cdot A},$$

where

$$A = \frac{\sqrt{2 \cdot \pi \cdot M} \cdot (2-\alpha)}{\sqrt{R} \, 2 \cdot \pi \cdot l \cdot (\beta+1/2) \cdot 2 \cdot \alpha},$$

and since

$$T_1'' = T_1 - \frac{2}{2-a}\delta\theta_1,$$

we have, by expansion and approximation,

$$\delta\theta_1 = \frac{Q \cdot \sqrt{T_1}}{p \cdot r \cdot A}\left(1 - \frac{Q \cdot \sqrt{T_1}}{p \cdot r_1 \cdot A \cdot (2-\alpha)T_1}\right) \cdot \cdot \cdot \quad (15)$$

Substituting for $\delta\theta_1$ and $\delta\theta_2$ from (15) in (4), therefore

$$Q \cdot \log_e \frac{(r_2 - \lambda_2)}{(r_1 + \lambda_1)} = 2 \cdot \pi \cdot k \cdot l \cdot (T_1 - T_2)$$

$$- 2 \cdot \pi \cdot k \cdot l \cdot \left(\frac{\sqrt{T_1}}{r_1} + \frac{\sqrt{T_2}}{r_2}\right) \cdot \frac{Q}{p \cdot A}$$

$$+ 2 \cdot \pi \cdot k \cdot l \cdot \left(\frac{Q}{p \cdot A}\right)^2 \left[\frac{1}{(2-\alpha) \cdot r_1^2} + \frac{1}{(2-\alpha') \cdot r_2^2}\right]. \quad (16)$$

If λ_1 and λ_2 are small compared with r_1 and r_2, the third term on the right-hand side of equation (16) is of negligible importance, and therefore

$$Q \cdot \log \frac{r_2}{r_1} = 2 \cdot \pi \cdot k \cdot l \cdot (T_1 - T_2)$$
$$- 2 \cdot \pi \cdot k \cdot l \cdot \left(\frac{\sqrt{T_1}}{r_1} + \frac{\sqrt{T_2}}{r_2} \right) \frac{Q}{p \cdot A} \cdot \quad (17)$$

For a range of pressures over which the mean free path is small compared with r_1 and r_2 equation (17) has been completely verified, and found to give a more accurate value of the accommodation coefficient than is contained in equation (8). As the pressure is decreased to a point where the gas becomes partially rarefied, equation (17) fails to represent the experimental facts.

The case of the heat transfer for a cylindrical distribution when the gas is partially rarefied has been made the subject of a special investigation by Mr. B. W. Ramsay, of the Imperial College of Science, who has applied equation (16) to calculate both the coefficient of accommodation and the molecular heat of the gas in terms of the experimental data associated with the heat transfer.

An account of the method, which is important from the aspect of its applicability to gases available only in small quantities and also to conditions of varying temperatures, will be published in the near future.

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XX. *Direct Determination of the Electrical Constants of Soil at Radio Frequency. By* BIMALENDU SEN-GUPTA, *M.Sc., and* S. R. KHASTGIR, *D.Sc. (Edin.), Dacca University* *.

1. *Introduction.*

IN connexion with the work on the ground attenuation of wireless waves undertaken at Dacca it was considered desirable to obtain a detailed knowledge of the

electrical properties of the Dacca soil for high-frequency alternating currents. The effective values of the electrical conductivity and of the dielectric constant of soil at radio frequency can be determined by applying Sommerfeld's theory of ground attenuation to radio field strength data ; and it is interesting to test how far these values agree with those obtained by direct laboratory methods under controlled conditions. It was realized that attention must be directed to the moisture-content of the soil under examination, and also to the fact that the electric constants of soil depend to an appreciable extent on the frequency of the alternating currents. Direct determinations of these constants were therefore undertaken for varying moisture-contents of the soil and for varying frequencies. Three different specimens of the Dacca soil were taken for examination. Specimens I. and III. were the sandy soil from the river-bed and the surface-soil of Ramna respectively. Specimen II. was dug out from a depth of 20 ft. underground.

Similar investigations have recently been carried out by Smith-Rose * in an elaborate manner. Ratcliffe and White also made direct measurements of the electrical constants of the soil. The method of Ratcliffe and White † was adopted in our investigations with a little modification.

2. *Theory of the Method.*

The method is essentially a variable-reactance method. The coil of a valve-maintained oscillator is coupled to that of the measuring circuit which comprises an inductance coil, an A.C. galvanometer, and a standardized variable condenser C. The soil-condenser C_S, placed in series with an auxiliary condenser of capacity C_1, is connected as shown in fig. 1 (a) in parallel with the variable condenser.

If ϵ is the dielectric constant and σ the electrical conductivity of the soil, and C_0 the value of the capacity of the soil-condenser when the soil is taken out, then, as shown in fig. 1 (b), the soil-condenser is equivalent to a perfect condenser of capacity $\epsilon . C_0$ shunted by a pure resistance R, where $R = \dfrac{1}{4\pi\sigma C_0}$. The current through

* Smith-Rose, Proc. Roy. Soc. A, cxl. p. 359 (1933).
† Ratcliffe & White, Phil. Mag. x. p. 667 (1930).

the soil in the condenser is not in phase with the E.M.F. across it. We can, however, resolve the current into a component I_R in phase with the E.M.F. and a component I_C in quadrature with it. If ϕ is the angle which I_R makes with the resultant current,

$$\tan \phi = \frac{I_C}{I_R}.$$

The current through the shunt resistance R is in phase with the E.M.F., so that I_R stands for the in-phase current
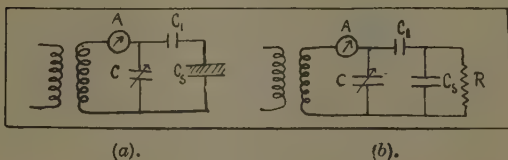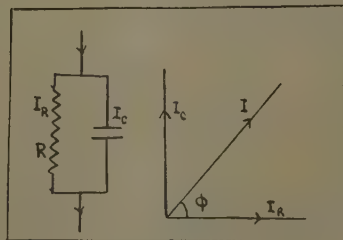
Fig. 1.

(a).   (b).

Fig. 2.

through R. The quadrature current I_C is the current through the condenser (see fig. 2).

If ω is the angular frequency of the alternating current,

$$\frac{I_C}{I_R} = \frac{R}{\dfrac{1}{\omega C_s}}.$$

Remembering $$R = \frac{1}{4\pi\sigma C_0},$$

we get $$\tan \phi = \frac{\omega}{4\pi\sigma} \cdot \frac{C_s}{C_0}.$$

By definition $$\epsilon = \frac{C_S}{C_0}, \quad \cdots \quad \cdots \quad (1)$$

so that $$\sigma = \frac{\epsilon \omega}{4\pi \tan \phi}. \quad \cdots \quad \cdots \quad (2)$$

The shunt resistance R is equivalent to a resistance r in series with the oscillatory circuit, such that

$$\frac{1}{r} = \omega^2 R \left[C_S + \frac{C_1 C_r}{C_1 + C_r} \right]^2, \quad \cdots \quad (3)$$

where C_r is the resonance value of the capacity C.

In the actual experiment by varying the tuning condenser C a resonance curve was obtained showing current in the oscillatory circuit against capacity. On both sides of C_r on the capacity-axis of the resonance curve the capacity values C_a and C_b, giving $\frac{1}{\sqrt{2}}$ times the resonance current, were marked out. The logarithmic decrement of the oscillatory circuit would be given by

$$\delta = \frac{\pi r}{\omega L} = \frac{\pi}{2} \frac{C_a - C_b}{C_R}, \quad \text{where} \quad C_R = C_r + \frac{C_1 C_S}{C_1 + C_S},$$

so that $$\frac{L\omega}{r} = \frac{2C_R}{C_a - C_b}. \quad \cdots \quad \cdots \quad (4)$$

Since $\omega^2 L C_R = 1$ for resonance, we would obtain from from (3) and (4)

$$\tan \phi = R\omega C_S = \frac{2}{C_a - C_b} \cdot \frac{C_R^2}{C_S} \cdot \frac{1}{\left[1 + \frac{C_1 C_r}{C_S(C_1 + C_r)} \right]^2}. \quad \cdot \quad (5)$$

The values of σ and ϵ would thus be determined from (1), (2), and (5).

3. *The Measurements of σ and ϵ.*

The soil-condenser was made up of a specially constructed parallel-plate condenser about 4 inches square, with a space of about 3 mm. The plates were made of brass. The top plate could be fixed very tightly sliding through slots in a pair of ebonite strips fixed on the opposite sides of the lower plate. The top-plate could be removed, and after introducing the soil under examination it could

be fixed very accurately in the original position. The plan and the elevation of the soil-condenser are shown in fig. 3.

In employing (1), (2), and (5) for the evaluation of σ and ϵ, the values of C_r, C_S, and C_0 were to be determined besides C_a and C_b. After having adjusted the condenser C at the value C_r for the tuning position without the soil-condenser, the latter, placed in series with the auxiliary condenser of known capacity C_1, was connected in parallel with the variable condenser. The circuit was then tuned. From the new tuning position $\dfrac{C_1 C_S}{C_1 + C_S}$ was determined. C_S was then calculated. C_0 was determined in

Fig. 3.
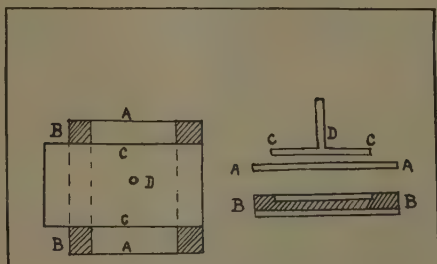
the same way after the soil had been taken out in terms of the standardized capacity.

The values of σ and ϵ were determined for two different frequencies $(1.875 \times 10^6$ and $.81 \times 10^6$ cycles/sec.) * for varying moisture-contents from 0 to 40 per cent. Whenever a sample of soil was taken out for electrical measurement a portion of this soil was placed in a heating chamber, and maintained at a temperature a little over 100° C. for about twelve hours, to determine the loss of weight by evaporation. The moisture-content was taken as the percentage of moisture to dry soil by weight.

Of the three specimens the soil taken from a depth of 20 ft. had decidedly low values of σ and ϵ. In all the specimens the rate of increase of both σ and ϵ was

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* These frequencies correspond to 160 m. and 370·4 m. wave-lengths of our University transmitter and of the V.U.C. station of the Indian State Broadcasting Co. respectively.

rapid in the beginning. A slight addition of moisture to the completely dry soil produced a very large increase in the values of σ and ϵ, each of which tended towards a constant value for large values of the moisture-content.

The changes of σ and ϵ with moisture-content for the two specimens (I. and II.) are graphically shown in figs. 4 and 5. The variation of σ and ϵ with frequency

Fig. 4.

SPECIMEN I
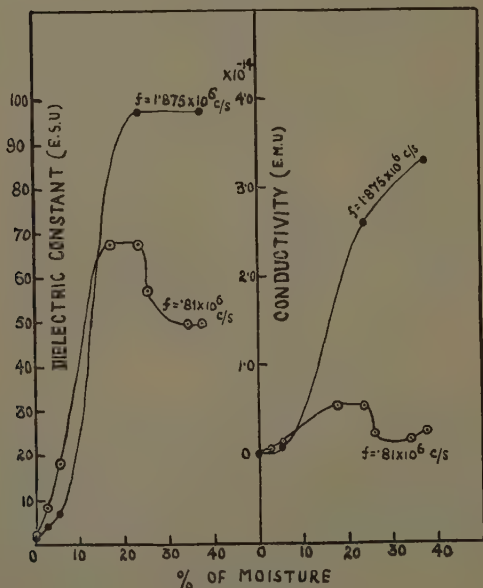
over the whole range ($\cdot 135 \times 10^6$ to $2 \cdot 7 \times 10^6$ cycles/sec.) was considerable. The results are illustrated in figs. 6 and 7. The values of conductivity in fig. 7 are shown in two stages. The inductance coils used were different in the two stages, and for each stage one and the same coil was employed. There appears a distinct peak in the conductivity-frequency curve at the point where the coil was changed. There has been also a slight irregularity in
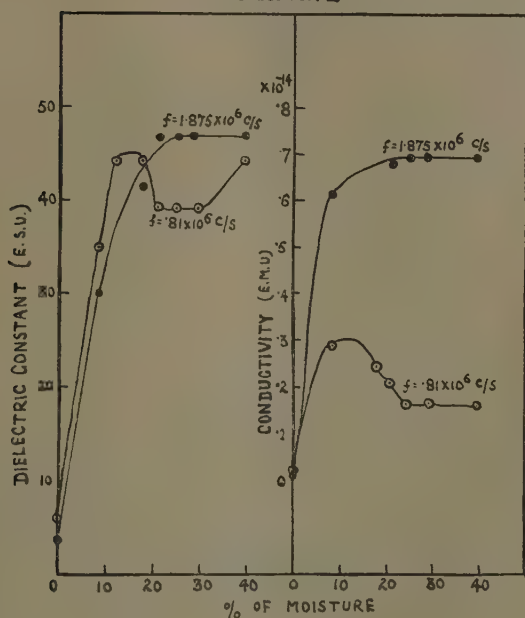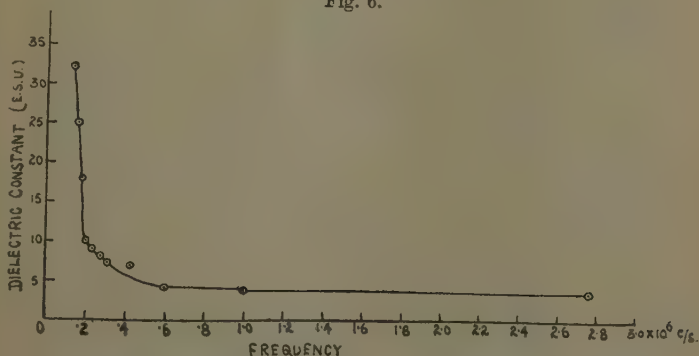
Fig. 5.

SPECIMEN II

Fig. 6.

the dielectric constant-frequency curve in this region.
It should be mentioned that Ratcliffe and White's
measurements revealed a peak in the conductivity-

frequency curve. Our actual experimental results are given in Tables I. and II.
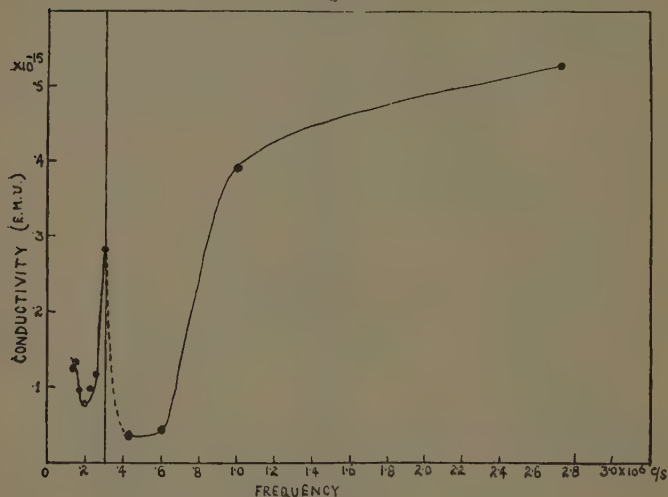
Fig. 7.

TABLE I.

	Specimen I.			Specimen II.		
Per cent. moisture.	ϵ (e.s.u.).	σ (e.m.u.).		Per cent. moisture.	ϵ (e.s.u.).	σ (e.m.u.).
A. Frequency $= 1\cdot875 \times 10^6$ cycles/sec.						
0	1·46	·006 × 10⁻¹⁴		0	3·52	·0185 × 10⁻¹⁴
2·2	4·28	·044	,,	8·1	30·0	·61 ,,
5·3	7·0	·068	,,	17·8	41·2	·59 ? ,,
						(not plotted).
23·5	97·9	2·63	,,	21·0	46·8	·68 ,,
37·5	97·9	3·32	,,	24·3	46·8	·69 ,,
				28·1	46·8	·69 ,,
				39·8	46·8	·69 ,,
B. Frequency $= ·81 \times 10^6$ cycles/sec.						
0	1·93	·002 × 10⁻¹⁴		0	5·64	·028 × 10⁻¹⁴
2·2	8·56	·053	,,	8·1	34·8	·29 ,,
5·3	18·6	·152	,,	17·8	43·9	·25 ,,
17·1	67·9	·57	,,	20·7	39·1	·21 ,,
23·5	67·9	·57	,,	24·3	39·1	·21 ,,
25·7	57·6	·25	,,	29·2	39·1	·16 ,,
34·1	49·9	·19	,,	39·8	43·9	·16 ,,
37·5	49·9	·28	,,			

TABLE II.

Dry soil *.

Frequency in cycles/sec.	ϵ (e.s.u.).	σ (e.m.u.).
$\cdot135 \times 10^6$	$32\cdot2$	$\cdot123 \times 10^{-15}$
$\cdot150 \times 10^6$	$25\cdot0$	$\cdot135 \times 10^{-15}$
$\cdot167 \times 10^6$	$18\cdot8$	$\cdot097 \times 10^{-15}$
$\cdot188 \times 10^6$	$10\cdot56$	$\cdot078 \times 10^{-15}$
$\cdot222 \times 10^6$	$9\cdot3$	$\cdot097 \times 10^{-15}$
$\cdot250 \times 10^6$	$7\cdot6$	$\cdot118 \times 10^{-15}$
$\cdot30 \ \times 10^6$	$7\cdot76$	$\cdot281 \times 10^{-15}$
$\cdot429 \times 10^6$	$7\cdot0$	$\cdot037 \times 10^{-15}$
$\cdot60 \ \times 10^6$	$4\cdot04$	$\cdot043 \times 10^{-15}$
$1\cdot0 \ \ \times 10^6$	$4\cdot0$	$\cdot391 \times 10^{-15}$
$2\cdot77 \ \ \times 10^6$	$3\cdot46$	$\cdot529 \times 10^{-15}$

4. *Summary and Conclusion.*

The electrical conductivity σ and the dielectric constant ϵ of three different specimens of Dacca soil were directly determined by a resonance method for various values of moisture content from 0 to 40 per cent. and for varying frequencies from $\cdot135 \times 10^6$ to $2\cdot72 \times 10^6$ cycles/sec. The values of σ and ϵ for the specimen of soil taken from a depth of 20 ft. were decidedly lower than those for the surface-soil. Both σ and ϵ were found to increase with the moisture-content, each tending towards a constant value for large values of the moisture-content. The variation of σ and ϵ with frequency was also considerable.

Smith-Rose's direct determinations of σ and ϵ with specimens of English soil gave distinctly larger values, whereas Ratcliffe and White's values were of the same order as those obtained by us.

It should be mentioned that the values of the electrical constants of the soil obtained by direct experiments agreed in their order of magnitude with the values deduced from the attenuation measurements.

Physics Department,
    Dacca University.
Sept. 21, 1935.

* The moisture-constant is less than 2 per cent.

XXI. *On the Refractivity and Dielectric Constant of Carbon Dioxide at High Pressures.* By P. O. JOHN, *Department of Physics, St. Joseph's College, Calcutta *.*

1. *The Lorentz Formula.*

AS is well known, the Lorentz formula $(n^2-1)/(n^2+2)\rho = C$, a constant, represents to a fair approximation the dependence of the refractive index of a medium on its density, even over such wide ranges as from the vapour to the liquid state. Accurate measurements, however, reveal a small but definite deviation from the formula. For example, in most aromatic compounds the expression $(n^2-1)/(n^2+2)\rho$, which we might call the Lorentz factor, decreases by about 4 or 5 per cent. as we pass from the vapour to the liquid. The deviations from the formula are even more marked when we calculate on its basis the variations of the refractive index of a liquid with either temperature or pressure. Taking again the aromatic liquids, the calculation gives about 10 per cent. higher values.

2. *The Anisotropy of the Polarization Field.*

These deviations from the Lorentz formula have been explained by Raman and Krishnan † in the following manner. It is well known from studies on light-scattering that molecules in general are optically anisotropic, and it is further known from X-ray and other studies that many molecules are also highly asymmetric in geometric shape. When such molecules are packed together densely as in a liquid, the distribution of the molecules surrounding any particular one in the medium will deviate considerably from spherical symmetry. As a consequence, the " polarization field " acting on the molecule will not be equal to $4\pi/3$ times the mean polarization of the medium per unit volume, as contemplated in the derivation of the Lorentz formula, but will be different for different directions of the electric vector of the incident light-wave, with reference to the molecule. In other words, as a consequence of the asymmetry of distribution of the polarizable matter surrounding any given molecule in

the medium, the polarization field acting on the molecule will be anisotropic. The magnitude of the anisotropy will evidently vary with the density of packing of the molecules, being nothing at very low densities, and reaching, for high densities, a certain limiting value characteristic of the geometric form of the molecules and the nature of their close-packing. The result will be (1) an apparent progressive variation of the optical anisotropy of the molecule with the density, and (2) a corresponding variation of the Lorentz factor.

3. *Experimental Verification.*

The general validity of the Raman-Krishnan theory has been established from various directions. The first result, namely, an apparent variation of the optical aniso- tropy of the molecule with density, is verified by studies on the depolarization factor of light-scattering *. Indeed, for liquids consisting of simple molecules like benzene, cyclohexane, hexane, etc., which may be assumed to have an axis of symmetry, these studies supply a method of calculating the anisotropy of the polarization field at different densities. On calculating the aniso- tropy of the polarization field in this manner, it is found that (1) in very dense media its magnitude is the same as we should expect from the known shapes of the molecules obtained from X-ray and other studies † ; (2) it explains quantitatively the variation of the Lorentz factor as we pass from the vapour state to that of liquid ‡ ; (3) the low values predicted by the Lorentz formula for the temperature and pressure variations in the refractive index of a liquid are also quantitatively explained by taking into account the changes in the anisotropy of the polarization field with the change in density accompanying the change in either temperature or pressure §.

The theory of the anisotropic polarization field explains also, in a satisfactory manner, similar discrepancies in the Lorentz formula when applied to the *dielectric behaviour* of a dense fluid ‖.

* C. V. Raman and K. S. Krishnan, Phil. Mag. v. p. 498 (1928).
† K. S. Krishnan and S. R. Rao, Ind. Journ. Phys. iv. p. 39 (1929).
‡ K. S. Krishnan, Proc. Roy. Soc. A, cxxvi. p. 155 (1929).
§ K. S. Krishnan, Proc. Roy. Soc. A, cxxvi. p. 155 (1929).
‖ K. S. Krishnan, Proc. Roy. Soc. A, cxxvi. p. 155 (1929) ; F. R. Goss, Journ. Chem. Soc. p. 1341 (1933), and p. 696 (1934).

4. *Scope of the Present Paper.*

In the present paper the influence of the anisotropy of the polarization field on the refractivity of a dense fluid is discussed from a different point of view. The anisotropy, *i. e.*, the excesses or deficits of the three polarization field factors from $4\pi/3$, should, as we mentioned in an earlier section, be a function of the geometrical form of the molecules, and the nature of their close-packing. The factors should be quite independent of the wave-length of the light used for the measurement of the refractive index.

Very extensive experimental data are available for the refractive index of carbon dioxide, over a large range of pressures, and for different wave-lengths, from the measurements of Phillips [*], and for its dielectric constant at different pressures from the recent measurements of Michels and Michels [†]. Since the CO_2 molecule possesses an axis of symmetry and the optical and dielectric constants of the molecule are known accurately, it will be a suitable substance for studying the influence of the anisotropy of the polarization field. It is proposed in this paper to follow the variation of the anisotropy with density, and in particular to verify whether for any given density the same degree of anisotropy explains the deviations from the Lorentz formula for the different wave-lengths.

5. *Expression for the Refractivity.*

We shall merely quote here the final expression for the refractivity of a dense fluid obtained by Raman and Krishnan. Let χ be the mean optical polarizability of the fluid per unit volume, per unit field (" in the medium ") of the electric vector of the light-wave ; $\chi=(n^2-1)/4\pi$, where n is the refractive index of the medium. When the direction of the electric vector E in the medium lies respectively along the three principal geometric axes of any given molecule, let $E(1+p_1\chi)$, $E(1+p_2\chi)$, and $E(1+p_3\chi)$ be the *actual* fields acting on the molecule, where p_1, p_2, p_3, are the polarization field factors ;

$$p_1+p_2+p_3=4\pi. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Further, let b_1, b_2, b_3 be the optical polarizabilities of the

molecule along the above three axes. Introducing the new quantities σ_1, σ_2, and σ_3, defined by the equations

$$\left.\begin{array}{l} \sigma_1 = p_1 - 4\pi/3, \\ \sigma_2 = p_2 - 4\pi/3, \\ \sigma_3 = p_3 - 4\pi/3, \end{array}\right\} \quad \ldots \ldots \quad (2)$$

Raman and Krishnan obtain the relation

$$\frac{n^2-1}{n^2+2} \cdot \frac{1}{\rho} = \frac{C}{1-\nu\Phi}, \quad \ldots \ldots \quad (3)$$

where *

$$C = \frac{4\pi}{3} \cdot \frac{N}{M} \cdot \frac{b_1+b_2+b_3}{3} \quad \ldots \ldots \quad (4)$$

$$\Phi = \tfrac{1}{3}(b_1\sigma_1 + b_2\sigma_2 + b_3\sigma_3), \quad \ldots \ldots \quad (5)$$

ν being the number of molecules per c.c., N the number per gram molecule, and M the gram molecular weight.

When the polarization field is isotropic, as at very low densities, or when the molecules are spherical, $\sigma_1 = \sigma_2 = \sigma_3 = 0$, and expression (3) reduces, as it should, to the Lorentz formula. Otherwise the expression on the left-hand side of (3), namely, the Lorentz factor, will vary with density, due to the variation of both ν and Φ appearing in the denominator on the right-hand side.

6. *Evaluation of the Constants.*

For the CO_2 molecule, which is generally regarded as linear with the C-atom in the centre, the line joining the atoms will be an axis of symmetry, and we may put $b_2 = b_3 (<b_1)$, and $p_2 = p_3 (>p_1)$, and the expression for Φ reduces to the simple form

$$\Phi = \tfrac{1}{3}(b_1 - b_2)\sigma_1. \quad \ldots \ldots \quad (6)$$

If the b's are known we can calculate from the experimental values of the Lorentz factor at different densities the corresponding values of Φ, and thence of σ_1. For carbon dioxide the b's can be calculated from the value of C, *i.e.*, of the Lorentz factor at very low densities, which gives $b_1 + 2b_2$, and the depolarization factor of light-scattering in the gaseous state, which gives

$$\frac{b_1 - b_2}{b_1 + 2b_2} = \sqrt{\frac{5r}{6-7r}}. \quad \ldots \ldots \quad (7)$$

* The constant C in Raman and Krishnan's paper has a slightly different significance, being equal to M/N times the C defined by our expression (4).

7. *Application to Carbon Dioxide at Different Densities.*

Phillips has measured with great accuracy the refractive indices of carbon dioxide at different densities, from that of the vapour to 0·74, for the three mercury lines λ5769–90, 5461, and 4358, at 34° C. The corresponding values of $(n^2+2)\rho/(n^2-1)$, $i.$ $e.$, of the reciprocal of the Lorentz factor, have been calculated by him, and are reproduced in the following table, in columns 2, 4,

TABLE I.

Density ρ.	$\lambda=5769$–90 Å.		$\lambda=5461$ Å.		$\lambda=4358$ Å.	
	$\dfrac{n^2+2}{n^2-1}\cdot\rho$.	$-\sigma_1$.	$\dfrac{n^2+2}{n^2-1}\cdot\rho$.	$-\sigma_1$.	$\dfrac{n^2+2}{n^2-1}\cdot\rho$.	$-\sigma_1$.
·73692	6·6620	1·0	6·6435	1·0	6·5580	1·0
·70549	6·6571	1·0	6·6382	1·0	6·5518	0·9
·66330	6·6515	0·9	6·6300	0·9	6·5445	0·9
·62083	6·6440	0·9	6·6222	0·8	6·5380	0·8
·57813	6·6368	0·8	6·6162	0·8	6·5322	0·7
·53566	6·6315	0·7	6·6112	0·7	6·5271	0·7
·49311	6·6280	0·7	6·6066	0·6	6·5222	0·7
·45063	6·6218	0·6	6·6029	0·6	6·5182	0·6
·40776	6·6192	0·6	6·5998	0·6	6·5158	0·6
·36509	6·6155	0·5	6·5964	0·5	6·5115	0·5
·32228	6·6129	0·5	6·5939	0·5	6·5090	0·4
·27904	6·6090	0·4	6·5893	0·4	6·5056	0·4
·23570	6·6067	0·3	6·5872	0·3	6·5040	0·3
·19239	6·6050	0·3	6·5858	0·3	6·5022	0·3
·14901	6·6020	0·1	6·5819	0·1	6·4988	0·1
·10526	6·6023	0·2	6·5823	0·1	6·4991	0·2
Gas at atmospheric pressure.	6·6005	0	6·5810	0	6·4975	0

and 6. The values in the last row, corresponding to normal gaseous densities, would, in our notation, be equal to $1/C$ (and are those obtained by Phillips by extrapolation from the values for the higher densities). Using these values of $1/C$ and the value $r=0.098$ for the depolarization factor of transverse light-scattering by the gas (for incident unpolarized light), which may, for our present purpose, be assumed to be nearly the same for all the three wave-lengths, the values of σ_1 were calculated, with

the help of the relations given in the previous section, and they are entered in columns 3, 5, and 7 of the table.

It is clear from Table I. (1) that for a given density the value of σ_1 is practically the same for all the three

Fig. 1.
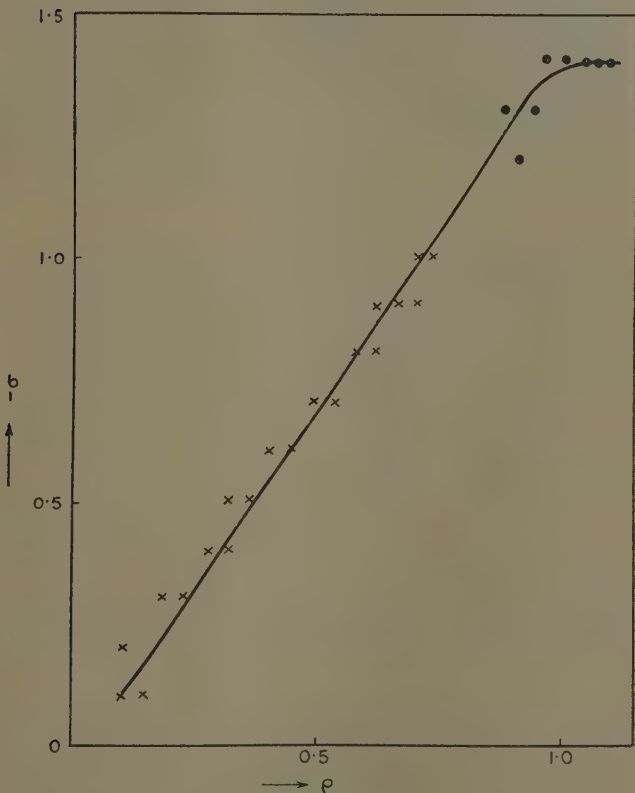
wave-lengths, and (2) that the numerical value of σ_1 (which may be taken as a measure of the anisotropy of the polarization field) increases progressively with the density. This is also brought out clearly in the graph (see fig. 1).

Both these results are just what we should expect.

8. *Dielectric Constant of Carbon Dioxide at High Pressures.*

The expressions for the dielectric constant of a dense liquid consisting of non-polar molecules will be very similar to (3), (4), and (5), except that the optical polarizabilities b_1, b_2, b_3 of the molecule should be replaced by the electric polarizabilities a_1, a_2, a_3. For the CO_2 molecule we may, as before, put $a_1 > a_2 = a_3$. $a_1 + 2a_2$ can, of course, be readily obtained from the dielectric constant for the gas, just as $b_1 + 2b_2$ is obtained from its refractivity. The difference $a_1 - a_2$, however, is not directly obtained as $b_1 - b_2$ is, but may be obtained in-

TABLE II.

Pressure in atmospheres.	ρ.	$\dfrac{K+2}{K-1} \cdot \rho$.	$-\sigma_1$.
970	1·113	5·77	1·7 (?)
812	1·083	5·74	1·4
700	1·061	5·74	1·4
588	1·035	5·74	1·4
476	0·999	5·74	1·4
364	0·968	5·73	1·4
295	0·936	5·72	1·3
247	0·909	5·71	1·2
194	0·876	5·72	1·3
	gas.	5·63	0

directly in either of the following ways : (1) we may assume that $a_1/a_2 = b_1/b_2$, and thus obtain

$$a_1 - a_2 = (a_1 + 2a_2) \times \frac{b_1 - b_2}{b_1 + 2b_2} \quad \ldots \quad (8)$$

Or (2) from the Kerr constant of carbon dioxide gas, which has been measured by Szivessy * and by Stuart and Volkmann †, and we may calculate the value of $(a_1 - a_2)(b_1 - b_2)$ and thence obtain $(a_1 - a_2)$. The two methods give practically the same values for $(a_1 - a_2)$.

The values of σ_1 at different densities can now be calculated in the same manner as in the optical case, and the calculated values are given in Table II. We should

* *Zeits. Phys.* xxvi. p. 323 (1924).
† *Zeits. Phys. Chem.* xvii. p. 429 (1932).

mention here that at these high pressures the measurement of dielectric constant is more difficult, and is much less accurate, than the measurements of refractivity.

The density range over which the above dielectric constant data extend does not overlap with the range of the refractivity measurements, so that it is not possible to compare directly the values of σ_1 obtained from the two. But it will be seen from the graph in the figure, in which both the values are plotted together, that though the dielectric values of σ_1 do not plot as smoothly as the refractivity values, they form a natural extension of the latter. (In the graph the former values are indicated by dots and the latter by crosses.)

9. *Summary.*

The deviations from the Lorentz formula in representing the refractive and dielectric behaviour of carbon dioxide over a wide range of densities are discussed on the basis of the theory of the anisotropic polarization field in dense media put forward by Raman and Krishnan. It is found, in conformity with the predictions of the theory, (1) that the anisotropy of the polarization field increases progressively with increase in density, and (2) that, for any given density, the degree of anisotropy required to explain the deviations from the Lorentz formula is the same for different wave-lengths of the incident light.

In conclusion, I thank Professor K. S. Krishnan for suggesting to me the problem and taking great interest while working it out.

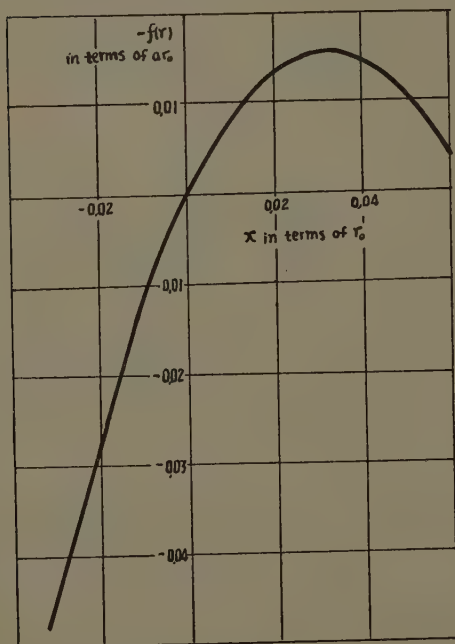### XXII. *On the Atomic Forces of Solid States.* *By* WENG WEN-PO [*].

PART III.

(9) LET us express the function $f(r)$ in an easily manageable form by setting

$$\frac{br_0}{a} = b' \quad \text{and} \quad \frac{cr_0{}^2}{a} = c',$$

and writing Δr as x,

$$f(r_0 + \Delta r) = -a\,\Delta r + b(\Delta r)^2 - c(\Delta r)^3$$

$$= ar_0 \left[-\frac{\Delta r}{r_0} + \left(\frac{br_0}{a}\right)\left(\frac{\Delta r}{r_0}\right)^2 - \left(\frac{cr_0^2}{a}\right)\left(\frac{\Delta r}{r_0}\right)^3 + \ldots \right]$$

$$= ar_0 \left[-\frac{x}{r_0} + b'\left(\frac{x}{r_0}\right)^2 - c\left(\frac{x}{r_0}\right)^3 + \ldots \right] \quad . \quad . \quad (35)$$

If we measure the force in units of ar_0 and the displacement in r_0 the function $f(r)$ will then have similar form for all metals and simple polar compounds as NaCl etc. It can be shown that as far as x/r_0 is less than 0·05 the c-term is not very appreciable. We can then plot $f(r_0 + x)$ in the region between $x/r_0 = -0·05$ and $x/r_0 = 0·05$. As a typical example the function $f(r)$ of silver, the value of br_0/a of which is near to 16, is plotted as shown in

the figure. This curve, in many respects, is in good accordance with the common conception.

(10) But the study of the nature of the function $f(r)$ is accompanied by a very unfavourable condition, for $f(r)$ represents a kind of force which originates from many ions instead of from a single ion. To overcome this difficulty we have to deal with atomic repulsion alone, since this, as we have mentioned in Part I., is effectually due to one neighbouring atom only.

If we assume the force to be composed of two parts, one attractive and the other repulsive, as imagined by Born [*], W. Bragg [†], Joffe [‡], and others, and the attraction is greatly due to the lattice energy of the ions, as treated by E. Madelung [§] and P. D. Ewald [‖], we have, by making the same kind of approximation as we have made in deriving equation (4), the attractional part as $-Ae^2/r^2$, where A is a certain constant. Let $R(r)$ be the repulsional part of $f(r)$; then

$$R(r) = f(r) + \frac{Ae^2}{r^2} \quad . \quad . \quad . \quad . \quad (36)$$

Substituting $r = r_0 + x$ into Ae^2/r^2, and expanding, we may write Ae/r^2 as

$$\frac{A}{r^2} = \frac{Ae^2}{r_0{}^2}\left[1 - 2\left(\frac{x}{r_0}\right) + 3\left(\frac{x}{r_0}\right)^2 - 4\left(\frac{x}{r_0}\right)^3 + \ldots\right].$$

Then, considering equation (35), equation (36) becomes

$$R(r_0 + x) = \frac{Ae^2}{r_0}\left[1 - \left(2 + \frac{ar_0{}^3}{Ac^2}\right)\left(\frac{x}{r_0}\right) + \left(3 + b'\frac{ar_0{}^3}{Ac^2}\right)\left(\frac{x}{r_0}\right)^2 \right.$$
$$\left. - \left(4 + c'\frac{ar_0{}^3}{Ac^2}\right)\left(\frac{x}{r_0}\right)^3 + \ldots,\right] \quad . \quad . \quad (37)$$

For the sake of convenience let $a' = ar_0{}^3/Ac^2$. Equation (37) becomes

$$R(r_0 + x) = \frac{Ac^2}{r_0{}^2}\left[1 - (2 + a')\left(\frac{x}{r_0}\right) + (3 + b'a')\left(\frac{x}{r_0}\right)^2 \ldots\right].$$
$$. \quad . \quad . \quad (38)$$

* *Handb. d. Phys.* xxiv. chapter 5 (1927).
† International Conference of Physics.—II. 'The Solid State of Matter,' p. 114 (1935).
‡ 'The Physics of Crystals,' p. 15 (1928).
§ *Physik. Zeitschr.* xix. p. 524 (1918).
‖ *Ann. d. Phys.* lxiv. p. 253 (1921).

To estimate the value of a' we introduce again the elastic constant as before.   Thus

$$a' = \left(\frac{3k^2}{Ac^2N_0^{\frac{4}{3}}}\right)\frac{\left(\dfrac{W}{\rho}\right)^{\frac{4}{3}}}{\beta_0}.$$

It will be very interesting to notice that a' for all metals and simple polar compounds are, just like b' or probably c' also, in the same order of magnitude.   This fact has been shown by Bridgman * by expressing $\dfrac{\left(\dfrac{W}{\rho}\right)^{\frac{4}{3}}}{\beta_0}$ in numerical values.

Concerning equation (38) we can summarize the following interesting features :—(1) The ratios of r_0 to the atomic size σ, calculated from Lindemann's hypothesis of fusion, are in the same order of magnitude for metals and simple polar compounds.   Or, we have $\rho\beta_0\overline{S}Tm$ to be roughly a constant.   (2) The values of a' which are proportional to $\dfrac{\left(\dfrac{W}{\rho}\right)^{\frac{4}{3}}}{\beta_0}$ are very roughly in the same order of magnitude.   (3) b' or $12k.\dfrac{1}{\rho\beta_0}\left[\dfrac{(\alpha_l T)}{\overline{S}(T)}\right]$ is also in the same order of magnitude. Here we may sensibly assume that the atomic repulsion is chiefly due to a combined effect of outmost shell of electrons and the inner core.   The so-called combined effect may be due to perturbation of atoms, as assumed by F. London † or Slater ‡, or due to static octopole, as assumed by Joffe §, or due to the residual field of the atoms, as described in the old fashioned octet hypothesis. Since the outmost electronic shells of all kinds of atoms are generally of similar appearance $R(r_0+x)$ will then be nearly a universal function if x is expressed in units of σ and R in units of e^2/σ^2, where σ is expected to be proportional to the diameter of the outmost shell of electrons. Hence the properties of equation (36) can be explained. As the outmost electronic shell of one solid has each its

* 'The Physics of High Pressure,' p. 167 (1931).
† *Zeits. f. Phys. Chem.* xi. p. 222 (1930).
‡ Phys. Rev. xxxvi. p. 57 (1930).
§ 'The Physics of Crystals,' p. 6 (1928).

own characteristic quantum condition, thus equation (38) is universal only when the order of magnitude is concerned. It can also be noticed that the constants a' and b' for elements of the same group, *e. g.*, alkaline metals, have better agreement.

We have already found that the collision hypothesis of fusion due to Lindemann is not a very successful hypothesis. In other words, the existence of a boundary sphere with diameter σ around an atom is still quite questionable. Let us now see how other hypotheses of fusion may be satisfactory.

(11) In case we feel that it is too artificial to believe the existence of a sharp boundary of an ion, we may assume the melting-point as the temperature at which the average maximum amplitude of oscillation along any one direction, *i. e.*, X_1/r_0, has reached such an extent that the atomic force $f(r_0+x)$ reaches a maximum. This view has been held by G. A. Tomlinson [*]. By the last assumption we have, at melting-point,

$$\frac{df(r_0+x)}{dx} = 0 ;$$

therefore

$$\frac{X_1}{r_0} = \frac{1}{2}\left(\frac{a}{br_0}\right).$$

To verify this we may substitute it into equation (16). Thus

$$\left(\frac{br_0}{a}\right) = \frac{3}{2}\sqrt{\frac{k}{\rho\beta_0 \bar{S}Tm}} . \quad . \quad . \quad . \quad (39)$$

The value so calculated can be compared with the value obtained by equation (29). In Table X. the values calculated from the two different equations are tabulated. From Table X. we see that the agreement is remarkably good considering the approximations we have so far made. Thus the present hypothesis of fusion seems to be on a quite rigid basis.

To reconcile the hypothesis with facts we have to abolish the collision hypothesis of fusion, but to retain

the idea of electronic shell with a relative size σ, so that we can still explain the properties of equations (38). Moreover the fact that the displacement at which $\dfrac{df}{dx} = 0$ bears a fixed ratio to r_0 can at the same time be explained. Then the value σ becomes, instead of the diameter of

TABLE X.

Metals.	br_0/a from eq. (29).	br_0/a from eq. (39) $\times 3/2$ *.	Metals.	br_0/a from eq. (29).	br_0/a from eq. (39) $\times 3/2$ *.
Al.............	17·6	15·8	Ca	10·8	11·3
Co	15·1	14·3	Fe	14·1	13·6
Ni	15·3	14·3	Cr........	12·4	15·0
Cu	16·8	14·9	Li	8·7	10·0
Ag	19·3	15·8	Na	9·7	10·9
Pt	20·9	19·0	K	10·2	9·9
Au	24·2	19·5	Rb	10·8	10·5
Pb	21·8	19·5	Cs........	9·2	10·1

* The factor 3/2 indicates a defect of the coefficient in equation (39).

Equation (29) $\dfrac{br_0}{a} = \dfrac{18\,k}{\rho\beta}\left[\dfrac{\alpha_\theta(\mathrm{T})}{\mathrm{S(T)}}\right]$.

Equation (39) $\dfrac{br_0}{a} = \dfrac{3}{2}\sqrt{\dfrac{k}{\rho\beta\;\mathrm{ST}_m}}$.

outermost electronic shell, the maximum diameter of the outmost electronic shell and also the relative size of the shell if such a shell is really in existence.

In conclusion, I am very glad to express my indebtedness to my cousin, Dr. Weng Wen-Hou, and my brother, Dr. Weng Wen-Lan, for their encouragement.

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XXIII. *Optical Constants of Copper-Nickel Alloys. By N. F.* MOTT, *M.A., Professor of Theoretical Physics in the University of Bristol* *.

THE optical constants of the copper-nickel series of alloys have recently been measured by Lowery, Wilkinson, and Bor †. The purpose of this note is to give a theoretical interpretation of the results achieved and to relate them to the magnetic properties of these alloys.

The copper-nickel alloys form a face-centred cubic lattice throughout the whole range. A theoretical discussion of their magnetic properties has been given by the author in a recent paper ‡. In metallic nickel there exists a band of allowed energy levels corresponding to the 3*d* state of an electron in the free atom. This band of levels would be completely full if it contained ten electrons per atom; actually in the metal there are 0·6 " positive holes " per atom in the band, which are responsible for the ferromagnetism, and which give a saturation moment of 0·6 Bohr magnetons per atom. The copper atom contains one more electron than the nickel atom; when copper is alloyed with nickel the extra electron goes into the 3*d* band, so that the saturation moment decreases linearly with concentration; at a composition of 60 per cent. copper it disappears, so that the *d* band is then full.

The figure below shows the absorption coefficient of Cu–Ni measured by Lowery for a wave-length of 5780 Å.U. It will be seen that the absorption coefficient of the alloys increases rapidly with increasing concentration of nickel while the alloy remains paramagnetic, but at a composition near to 40 per cent. Ni, where the ferromagnetism begins, the curve flattens out, and the absorption coefficient then remains roughly constant.

The wave-length 5780 Å.U. lies on the low frequency side of the absorption band of copper. The origin of this band will not concern us here; it may be due to the ionization of the 3*d* level of copper, or to the ejection of an *s* (conduction) electron to a higher state.

Only one explanation seems possible for the rapid rise in *nk* as nickel is added to copper. It must be due to absorption resulting from the ejection of electrons from the 3*d* shells of the nickel atoms. We should expect the energy *hν* required for this process to be less than that required to eject an electron from the *d* shell of copper. An estimate of it will be made below.
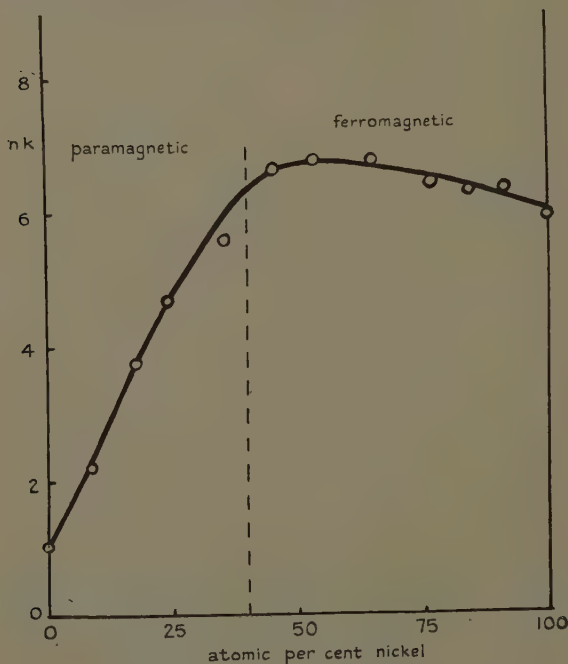
Absorption coefficient *nk* of Cu–Ni alloys.

We thus expect the absorption coefficient to rise linearly with increasing proportion of nickel. We have now to explain why in fact it only rises linearly as long as the alloy is not ferromagnetic. The explanation is as follows :—Up to a composition of 40 per cent. nickel the nickel ions contain, as we have seen, ten *d* electrons, forming, therefore, closed shells ; for greater compositions each nickel ion added gives one Bohr magneton to the

magnetic moment, and must therefore contain only nine d electrons. There would thus be, among 100 atoms of all kinds, 40 nickel atoms with full ions, the remainder of the nickel ions containing a " positive hole." These positive holes would of course move from atom to atom through the lattice.

Now it is natural to suppose that the work required to remove an electron from a closed d shell is considerably less than that required to remove one from a d shell containing only nine electrons; hence we conclude that only those ions which have no " positive hole " in them can contribute to the absorption for the wave-length considered. It follows that the absorption coefficient will only increase in the observed range.

The small increase in nk when copper is added to nickel may well be due to the high resistance of the copper-nickel alloys.

Finally, we shall attempt to estimate the low frequency limit of the absorption band. For nickel and for all alloys with up to 60 per cent. copper, the work required to remove an electron from the d band to the s band is zero (*cf.* Mott, *loc. cit.* fig. 2). Actually the poor reflecting power of nickel in the infra-red suggests that the absorption band does in fact extend to quite long wave-lengths [*].

For alloys containing less than 40 per cent. of nickel, however, the highest occupied s state has higher energy than the $3d$ state of nickel. Since the number of s electrons is $1-x$ per atom, the energy of the former state is, according to the formula due to Sommerfeld

$$(1-x)^{\frac{2}{3}}E_{\mathrm{F}}, \quad E_{\mathrm{F}} = \frac{h^2}{8m}\left(\frac{3}{\pi\Omega_0}\right)^{\frac{2}{3}} = 7\cdot1 \text{ e.v.}$$

where Ω_0 is the atomic volume and $x:(1-x)$ the ratio of the number of nickel atoms to those of copper. For $x=0\cdot4$ this will be just equal to the energy of the d shell. Therefore the work required to remove a d electron is

$$\{(1-x)^{\frac{2}{3}}-(0\cdot6)^{\frac{2}{3}}\}E_{\mathrm{F}},$$

* The poor reflecting power can also be accounted for by the Hagen-Rubens formula in terms of the measured electrical resistance; but, as pointed out by Mott and Zener, Proc. Camb. Phil. Soc. xxx. p. 249 (1934), it is unlikely, on theoretical grounds, that this formula is a good approximation for wave-lengths less than 30 μ. A formula taking into account the inertia of the electrons, but neglecting photo-electric absorption, gives much higher reflecting power.

which will give the low frequency limit of the absorption band. For instance, for an alloy containing 10 per cent. of nickel it is

$$\{(0.9)^{\frac{2}{3}} - (0.6)^{\frac{2}{3}}\} E_r = 1.57 \text{ e.v.,}$$

corresponding to a wave-length of 0.8μ.

XXIV. *The Thermal Expansion of the Crystal Lattices of Cadmium, Osmium, and Ruthenium. By* Prof. E. A. Owen, *M.A., D.Sc., and* E. W. Roberts, *M.Sc., University College of North Wales, Bangor* *.

A FOCUSSING camera suitable for use at high temperatures provides a convenient means of measuring the coefficients of thermal expansion of metals and alloys ; for the purpose only a small amount of material is required, and values of the parameters can be obtained when the material is heated to any temperature *in vacuo*. The camera employed in this laboratory and the method of procedure have already been described elsewhere †. The method is particularly applicable to examine the thermal expansion of metals possessing hexagonal structure such as the three elements now under investigation, as it gives directly the coefficients of expansion along and perpendicular to the hexagonal axis.

The sources of error in the method have previously been considered. It is possible without much difficulty to obtain an accuracy of 1 in 10,000 in the determination of the parameters of cubic lattices ; this accuracy is somewhat more difficult to obtain with hexagonal lattices, but if the measurements are checked by employing different methods, as explained in a previous paper ‡, on the measurement of the parameters of hexagonal lattices, it is possible to attain an accuracy which exceeds the above figure.

The temperature measurement must be carefully carried out. The nickel-nichrome thermocouple used for the

purpose was frequently calibrated during the course of the work. Checked against the parameter of silver at different temperatures, it was found that in general the temperatures were correct to within 1 per cent.

(1) CADMIUM.

(a) *Parameters of Pure Cadmium at Ordinary Temperature.*

The material used in the investigation had a purity not less than 99·9 per cent. Filings were taken and annealed to remove distortion produced by filing. The spectral lines obtained with these filings were rather weak ; better lines were obtained by rolling the filings to form a thin foil, 0·1 mm. thick. The contact between the foil and the thermocouple sheet on which it was mounted was found to improve by introducing a thin layer of adhesive between them. The lattice parameters obtained with the foil at different temperatures were found to agree with those obtained with the filings, showing that there was no appreciable temperature drop in the foil.

Of the several radiations tried the lines obtained with a nickel target were strongest ; this radiation was used for all the high temperature exposures. The values of the wave-lengths of nickel employed in the calculations were $K_{\alpha_1} = 1·65450$ Å. and $K_{\alpha_2} = 1·65835$ Å.* With this radiation reflexions from planes $21\bar{3}3$, $30\bar{3}0$, and $20\bar{2}5$ were obtained on the film. Owing to the low melting-point of cadmium the decrease in intensity of the lines with increasing temperature was very marked. In consequence of this the accuracy of the measurement of the arcs was less at the higher temperatures.

Particular attention was paid to the determination of the lattice parameters of cadmium at room-temperature, as the determinations made previously in this laboratory differed slightly from the figure accepted by Neuburger †. For this purpose the material was prepared for examination in three forms. In addition to the " powder foil " and filings above mentioned, specimens were prepared by sublimation *in vacuo* at a temperature slightly below the melting-point.

* Siegbahn, ' Spectroskopie der Rontgenstrahlen,' 2nd ed.
† *Zeits. Krist.* lxxxvi. p. 395 (1933).

The first specimen tried consisted of filings annealed at 300° C. for 1 hour, which had been prepared and used by another worker about eighteen months previously, when spectral lines of uniform intensity were obtained. On this occasion the filings were not submitted to any further heat treatment and the lines were found to be " spotty," showing that the crystals had been growing in the specimen even at room-temperature. This effect is typical of a soft metal, and has been observed frequently with cadmium *.

Fresh filings and " powder foils " were prepared all of which yielded satisfactory lines ; the lines obtained with the foil were somewhat stronger in relation to the background than those obtained with filings.

Some interesting facts came to light when preparing sublimated cadmium. The material sublimes rapidly *in vacuo* at temperatures between 200° C. and 300 C. From Egerton's vapour pressure equation † for solid cadmium it may be calculated that at 200° C. the vapour pressure of cadmium is 0·001 mm. of mercury. This was approximately the pressure of the residual air in the evacuated chamber. When the cadmium was heated in the chamber at a temperature between 200° C. and 300° C. it rapidly disappeared and was deposited on the walls.

When preparing a specimen for the X-ray camera the cadmium deposited directly on the thermocouple backing sheet, which was mounted a few centimetres above the heated cadmium filings. A good vacuum in the chamber was essential, and also it was found best to perform the sublimation quickly at a temperature just below 300° C. By keeping this temperature constant, the nature of the deposit could be altered by varying the distance between the sheet on which the cadmium was heated and the backing sheet on which the vapour was deposited. When this distance was about 5 to 6 cm., so that the surface of the backing sheet was relatively cool, the deposit was greyish in colour ; it presented a matt surface which contained exceedingly small crystals. By reducing the distance to about 3 cm., thereby increasing the temperature of the backing sheet, a whitish deposit consisting of crystals which were now of larger size, was

* *Cf.* Jenkins, Journ. Inst. Metals, xlv. p. 330 (1931).
† Journ. Chem. Soc. London, cxxiii. p. 3024 (1923).

obtained. The thickness of a deposit was estimated by depositing material at the same time on an aluminium sheet placed alongside the backing sheet. An examination of this deposit, which could with care be removed for measurement, showed that in general the deposits employed in these experiments varied in thickness from 0·03 to 0·15 mm.

In view of previous results obtained with sublimated cadmium by other investigators it was considered desirable as a first step to establish definitely whether the structures of ordinary cast cadmium and sublimated cadmium were the same. Spectrum photographs taken with the two specimens were found to be identical, the structure of each being close-packed hexagonal.

When the specimens were examined on the precision camera the lines obtained with sublimated cadmium were well defined, but the spectra revealed an interesting orientation effect. For example, with cadmium filings the doublet obtained by the reflexion of nickel radiation from the plane (3030) was well marked, but with sublimated cadmium it had almost disappeared. The plane (3030) is parallel to a prism face, and since this set of planes is not reflecting, the crystallites in the sublimated layer must be set with their hexagonal axes parallel to the direction of the incident X-ray beam, that is, normal to the backing sheet. The basal planes are thus in the plane of the surface of the sheet, in the same manner as they are found in a rolled sheet of metal possessing hexagonal structure. This orientation effect has previously been reported by Volmer †. He examined the orientation of the crystals by means of a goniometer and showed that the basal planes of the hexagonal crystals were perpendicular to the direction of the beam of vapour. The present X-ray observations confirm this result.

Table I. contains the results obtained for the parameters of cadmium at room-temperature, the parameters having all been corrected to 18° C.

These values agree well with those of Preston† namely, $a = 2\cdot9724$ Å. and $c = 1\cdot8854$. Assuming that the mass of an atom of unit atomic weight is $1\cdot649 \times 10^{-24}$ gm. and the atomic weight of cadmium is 112·41, the density of

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* *Zeits. f. Physik*, v. p. 31 (1921).
† Appendix : Jenkins, Journ. Inst. Metals, xlvi. (1931)

cadmium at 18° C. becomes 8·646 gm. per c.c., which agrees with the value 8·648 gm. per c.c. given in the International Critical Tables.

(b) *Thermal Expansion of Cadmium.*

Nickel radiation was found the most suitable for the purpose of examining the thermal expansion of cadmium. All the exposures were made when the camera was mounted in an evacuated enclosure within which the pressure was maintained at a value not greater than 0·001 mm. of mercury. The backing sheet behind the specimen was in

TABLE I.

Film. no.	Form of specimen.	Radia- tion.	a (Å.)	c.
1......	Powder-foil.	Ni	2·9725	1·8851
2......	,,	Cu	2·9724	1·8850
3......	,,	Fe	2·9725	1·8852
6......	,,	Ni	2·9722	1·8852
7......	,,	Cu	2·9722	1·8853
10......	,,	Ni	2·9721	1·8856
15......	,,	Ni	2·9722	1·8851
39......	Filings.	Ni	2·9723	1·8853
78......	,,	Ni	2·9723	1·8854
25......	Sublimated.	Ni	2·9722	1·8855
26......	,,	Ni	2·9725	1·8852
55......	,,	Ni	2·9723	1·8855
56......	,,	Ni	2·9721	1·8858
40......	Backing sheet of Cd.	Ni	2·9723	1·8853

Mean values at 18° C. after correcting for refractivity :
$a = 2·9723_8$ Å. ; $c = 1·8853_2$; $ac = 5·6038_8$ Å.

each case 3 mm. thick, and the thermocouple was let into its front face.

(i.) *Sublimated Cadmium.*

The first specimen examined was prepared by sublimation on to the clean surface of a copper backing sheet, the thickness of the deposited layer being about 0·05 mm. The results of the measurements are summarized in Table II.

The table contains also the results obtained with layers of sublimate 0·03 mm. and 0·12 mm. thick respectively. These additional specimens were tried to

TABLE II.

Cadmium Sublimate on Copper Backing Sheet. Ni Radiation. Reflecting Planes (2133) and (20$\bar{2}$5). Chamber evacuated.

No. of film.	Temp. °C.	Base side, a (Å.).	Axial ratio, c.	Height ac (Å.).	Atomic volume (Å.)³.
(a) Specimen 0·05 mm. thick.					
34......	49	2·9746	1·8877	5·6153	21·515
33... ..	76	2·9763	1·8891	5·6225	21·567
30......	100	2·9783	1·8903$_5$	5·6304	21·626
50. ...	106	2·9786	1·8903$_5$	5·6307	21·632
35......	127	2·9804	1·8917	5·6381	21·686
29......	155	2·9823	1·8928	5·6449	21·740
31......	187	2·9849	1·8939	5·6531	21·809
(b) Specimen 0·12 mm. thick.					
58......	85	2·9771	1·8895	5·6251	21·587
57......	123	2·9795	1·8916	5·6360	21·665
(c) Specimen 0·03 mm. thick.					
62......	109	2·9784$_5$	1·8907$_5$	5·6315	21·632
63......	176	2·9835$_5$	1·8934	5·6490	21·774

find if an appreciable temperature gradient existed in the sublimated cadmium specimens. From the curves shown in figs. 1 to 3 it was concluded that the temperature gradient in all the samples was negligible, since all the points fall approximately on the same curve.

The last specimen, thickness 0·03 mm., is of interest, as it was the only one out of about fifteen specimens prepared by sublimation which gave reflexions from the (3030) planes of sufficient intensity to be measured.

Fig. 1.

THERMAL EXPANSION OF CADMIUM (SUBLIMATED)
PARALLEL TO THE AXIS

HEIGHT (Å)

⊕---0·03 MM. CADMIUM ON COPPER BACKING SHEET
⊙---0·05 MM. " "
⊕---0·12 MM. " "
□---0·05 MM. CADMIUM ON CADMIUM BACKING SHEET
△---0·05 MM. CADMIUM ON INVAR BACKING SHEET

TEMPERATURE (°C)

Fig. 2.

THERMAL EXPANSION OF CADMIUM (SUBLIMATED)
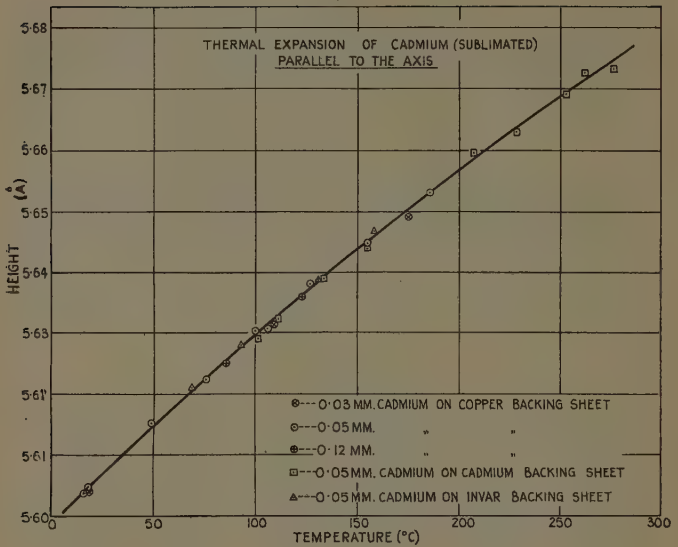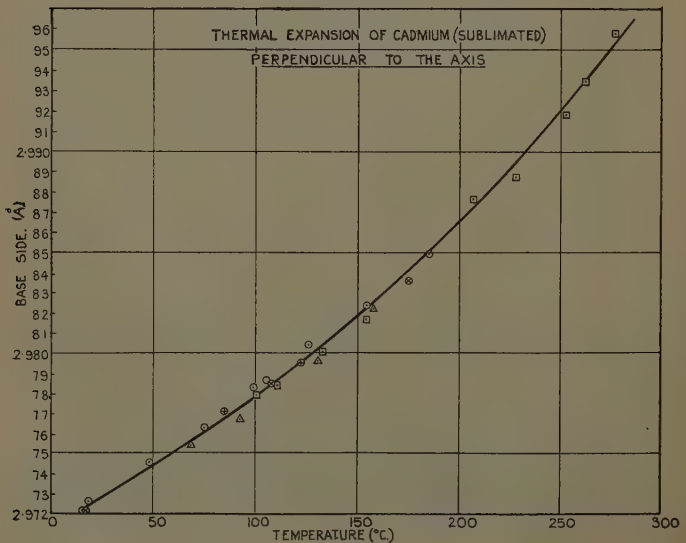PERPENDICULAR TO THE AXIS

BASE SIDE, (Å)

TEMPERATURE (°C.)

When attempts were made to extend the temperature range beyond 200° C., several difficulties were met, the chief of these being the sublimation of cadmium *in vacuo* above this temperature. This difficulty was overcome by filling the chamber with nitrogen and keeping the pressure throughout an exposure about the same as that of the atmosphere. With this arrangement it was possible to take photographs up to 280° C.

At these high temperatures another source of trouble appears owing to the diffusion of cadmium into the material of the backing sheet. With copper this diffusion

Fig. 3.

THERMAL EXPANSION OF CADMIUM (SUBLIMATED)
ATOMIC VOLUME.
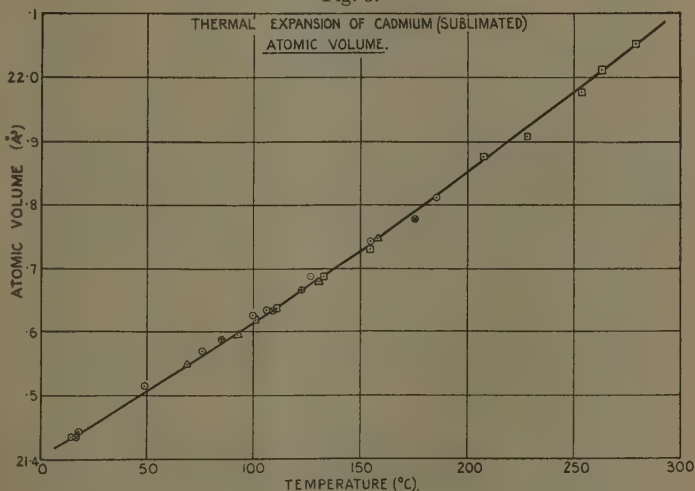
was marked. It was necessary, therefore, to deposit the cadmium on a pure cadmium backing sheet. It was also considered possible that, even if the cadmium did not diffuse into the material of its mounting, distortion of the cadmium lattice might be produced on account of the relative expansion of the two materials, which after sublimation were in intimate contact. By using a pure cadmium backing sheet these sources of error were eliminated.

The results obtained at the highest temperatures are summarized in Table III. and are included in the graphs in figs. 1 to 3. All the points fall on fairly smooth curves.

TABLE III.

Cadmium Sublimate on Cadmium Backing Sheet. Ni
Radiation. Reflecting Planes (21$\bar{3}$3) and (20$\bar{2}$5).
Chamber filled with Nitrogen.

No. of film.	Temp. °C.	Base side, a (Å.).	Axial ratio, c.	Height, ac (Å.).	Atomic volume (Å.)^3.
84......	208	2·9876	1·8944	5·6597	21·874
76......	229	2·9887	1·8949	5·6633	21·904
89.......	254	2·9918	1·8950	5·6695	21·974
85	263	2·9934$_5$	1·8952	5·6732	22·012
86......	279	2·9958	1·8939	5·6738	22·050

(ii.) *Cast Cadmium.*

A slight difference in the expansion of sublimated and
cast cadmium was observed, the sublimated material
expanding more readily than the cast ; this matter needs
further investigation. We give in this paper the results
obtained with sublimated cadmium, which is material
of a high degree of purity.

Final Results obtained with Cadmium.

Assuming $x_{t+20}=x_{20}(1+\alpha t+\beta t^2+\gamma t^3)$, values of the
coefficients α, β, and γ for the curves were calculated and
are included in Table IV.

TABLE IV.

Expansion Coefficients of Cadmium (Sublimated).

	$10^6 \alpha$.	$10^9 \beta$.	$10^{12} \gamma$.
Base side	21·7	− 3·$_8$	13$_4$
Height..............	55·8	−15·$_0$	−4$_7$
Atomic volume	95·1	38·$_4$	5$_9$

From these results values of the thermal coefficient
$\left(\dfrac{1}{x_{20}}\dfrac{dx}{dt}\right)$ at different temperatures were obtained.

As a check on the curves, the mean thermal coefficient
of linear expansion as determined from the atomic volume

curve is compared with the value calculated from the expression $(\alpha_{\shortparallel} + 2\alpha_{\perp})/3$ when the separate values of the coefficients $\alpha_{\shortparallel}$ and $\alpha_{\perp}$ are employed. There is in general a slight difference between these two values which shows that a certain latitude must be allowed in the values of the coefficients.

A determination of the thermal coefficients of expansion of cadmium along and perpendicular to the hexagonal axis was made by Gruneisen and Goens *, who used single crystal rods and worked between temperatures of $-220°$ C. and $+60°$ C. Their results, together with those now obtained over the range from $20°$ C. to $280°$ C.,

TABLE V.

Temp. °C.	$10^6\alpha_{\perp}$.	$10^6\alpha_{\shortparallel}$.	10^6 (vol/3).	10^6 $(\alpha_{\shortparallel} + 2\alpha_{\perp})3$.	Mean linear co-efficient.
20	21·7	55·8	31·7	33·1	32·4
60	22·1	54·1	32·8	32·8	32·8
100	23·7	52·3	34·1	33·2	33·6
150	27·5 .	49·2	36·0	34·7	35·3
200	33·3	45·5	38·2	37·4	37·8
240	39·5	42·1	40·2	40·4	40·3
280	46·9	38·4	42·4	44·1	43·2

with sublimated cadmium are plotted in fig. 4. It will be seen that, although the present values between $20°$ C. and $60°$ C. are slightly higher than those of Gruneisen and Goens, the forms of the curves follow approximately those to be expected by extrapolation of these curves

The thermal coefficient of expansion of cadmium parallel to the hexagonal axis after reaching a maximum value at about $-160°$ C. decreases continuously between this temperature and $280°$ C., the highest temperature now reached. The coefficient parallel to the axis, on the other hand, increases over the whole range of temperature investigated, namely, from $-220°$ C. to $280°$ C. The curves show that at about $250°$ C. cadmium is isotropic ; whereas below this temperature the expansion along is

* *Zeits. f. Physik*, xxix. p. 141 (1924).

greater than at right angles to the axis, above this temperature the reverse is the case. It would be of interest to see whether other directional properties, such as, for instance, electrical conductivity, also indicate isotropy at this temperature. Possibly this has already been done, but we have failed to find reference to it in the literature.

In conclusion, it may be stated that no evidence was found of the allotropic change at 60° C. suggested by Cohen * and Greenwood † and refuted by Preston ‡ as a result of an X-ray investigation of rolled cadmium.

Fig. 4.
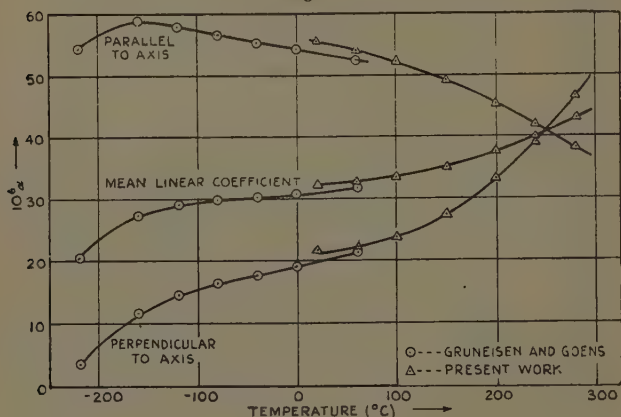
(2) OSMIUM.

The purity of the material available was not less than 99·8 per cent. A small lump was crushed and ground into powder which was annealed for five hours at 1000° C. to remove the effect of cold work.

The lines in the photographs were not intense, but their intensity did not vary much with temperature. Nickel radiation gave two doublets of fair density and copper radiation one doublet reasonably strong. Exposures were made at temperatures ranging from 20° C. to 600° C. using both copper and nickel radiations. From measure-

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* Trans. Faraday Soc. x. p. 216 (1914).
† Trans. Faraday Soc. xvii. p. 3 (1921).
‡ *Loc. cit.*

ments of the photographs the values of the parameters and atomic volume were calculated for each temperature. These were plotted against temperature, and from the curves, values of the parameters at definite temperatures were chosen which were utilized in the formula

$$\alpha_{t_1 t_2} = \frac{1}{x_{20}} \left(\frac{x_{t_2} - x_{t_1}}{t_2 - t_1} \right)$$

to calculate the mean coefficients between the temperatures t_1 and t_2 where $t_2 - t_1 = 100°$ C., x_t being the value of the parameter considered at $t°$ C. The mean values of the parameters of osmium at 18° C. are $a = 2·7300$, $c = 1·5788$, $ac = 4·3101$.

The values of the mean coefficients of expansion of osmium at a number of mean temperatures between 50° C. and 550° C. along and at right angles to the hexagonal axis together with the mean linear expansion coefficient, are collected in Table VI.

TABLE VI.

Mean Coefficients of Thermal Expansion of Osmium.

Temp. °C.	$\alpha_{\parallel} \times 10^6$	$\alpha_{\perp} \times 10^6$.	Mean linear coefficient $\times 10^6$.
50	5·9	4·0	4·8
150	6·2$_5$	4·2	5·0
250	6·6$_5$	4·5	5·3
350	7·1.	4·9	5·6$_5$
450	7·6$_5$	5·3	6·1$_5$
550	8·3$_5$	5·8$_5$	6·8$_5$

(3) RUTHENIUM.

A small quantity of chemically pure ruthenium was available, and after annealing *in vacuo* for three hours at 1000° C. very strong and well-defined reflexion lines were obtained. Nickel and copper radiations were used to take the photographs ; the former gave two and the latter four doublets, all of which were utilized to evaluate the parameters. Exposures were made at different temperatures in the range between 20° C. and 600° C. Owing to the high melting-point of the metal there was very little falling off in the intensity of the lines. The values of the

parameters calculated from the measurements of the
films were plotted against temperatures, resulting in
smooth curves from which the values of the parameters
at intervals of temperature of 50° C. were taken.   These
were used as in the case of osmium to calculate the mean
thermal coefficients along and at right angles to the hexa-
gonal axis.   The values of the parameters of ruthenium
at 18° C. are :—$a - 2·6986$ Å., $c = 1·5834$, $ac = 4·2730$.

The mean linear coefficient of expansion of osmium and
ruthenium at 50° C., namely, $4·8 \times 10^{-6}$ and $6·9 \times 10^{-6}$,
are both lower than the mean values $5·7 \times 10^{-6}$ and
$8·5 \times 10^{-6}$ between 10° C. and 90° C. given by Fizeau *

TABLE VII.

Mean Coefficients of Thermal Expansion of Ruthenium.

Temp. °C.	$\alpha_{\parallel} \times 10^6$.	$\alpha_{\perp} \times 10^6$.	Mean linear coefficient $\times 10^6$
50	8·8	5·9	6·9
150	9·3	6·1$_5$	7·2$_5$
250	9·8$_5$	6·4$_5$	7·6
350	10·4	6·8	7·9$_5$
340	11·0	7·2	8·3$_5$
550	11·7	7·6$_5$	8·7$_5$

for the two elements, and determined by the optical
interference method.   When it is reflected that Fizeau
carried out his measurements two-thirds of a century
ago with material which was probably not so pure as
that now available, the agreement between the two
determinations is tolerably good.   We have not been
able to trace any determinations of the thermal expansion
of osmium and ruthenium since Fizeau carried out his
classic experiments.

Summary.

The thermal expansions of the   crystal lattices of
cadmium, osmium, and ruthenium along and at right
angles to the hexagonal axis were measured by the X-ray
method.

* *Comptes Rendus*, lxviii. p. 1125 (1869).

Cadmium was examined in the cast and in the sublimated forms. Both forms possessed identical close-packed hexagonal structures, the parameters of which at 18° C. were $a = 2.9723_8$ Å. and $c = 1.8853_2$. These give a crystal density of 8·646 gm. per c.c.

The crystals in sublimated cadmium showed a preferred orientation, the basal planes being perpendicular to the direction of the vapour stream. This confirms Volmer's observations.

The thermal expansion of cadmium was examined over the range of temperature from 20° C. to 280° C. The thermal coefficients in directions along and at right angles to the hexagonal axis, together with the mean linear coefficient at different temperatures, were calculated. These results are combined with those of Grüneisen and Goens, who measured the thermal coefficients of cadmium in the two directions mentioned for single crystal rods between temperatures of −200° C. and +60° C.

The thermal coefficient of expansion of cadmium parallel to the hexagonal axis after reaching a maximum value at about −160° C. decreases continuously between this temperature and 280° C.

The thermal coefficient parallel to the axis increases over the whole range of temperature from −220° C. to 280° C.

At about 250° C. cadmium is isotropic; below this temperature the expansion along is greater than at right angles to the axis, above this temperature the reverse is the case.

No evidence was found of an allotropic change at 60° C. reported by some investigators.

The thermal expansions of osmium and ruthenium parallel and perpendicular to the hexagonal axis were measured over a range of temperature from 20° C. to 600° C.

For osmium the values of $\alpha_{\parallel}$ at 50, 150, 350, and 550° C. are 5·9, 6·3, 7·1, and $8·3_5 \times 10^{-6}$; the values of $\alpha_{\perp}$ at the same mean temperatures are 4·0, 4·2, 4·9, and $5·8_5 \times 10^{-6}$; the mean linear coefficients at the same temperatures are 4·8, 5·0, $5·6_5$, and $6·8_5 \times 10^{-6}$ per °C.

For ruthenium the values of $\alpha_{\parallel}$ at mean temperatures of 50, 150, 350, and 550° C. are 8·8, 9·3, 10·4, and $11·7 \times 10^{-6}$; the values of $\alpha_{\perp}$ at the same mean temperatures are 5·9, 6·15, 6·8, and $7·6_5 \times 10^{-6}$; the mean linear

coefficients at the same mean temperatures are $6·9$, $7·2_5$, $7·9_5$, and $8·7_5 \times 10^{-6}$ per °C.

We wish to express our indebtedness to the Department of Scientific and Industrial Research for a grant which enabled us to carry out the work.

XXV. *On the Thermal Expansion of Beryllium. By* Prof. E. A. OWEN, *M.A., D.Sc., and* T. LL. RICHARDS, *B.Sc., University College of North Wales, Bangor* *.

THE lattice constants of beryllium (99·8 per cent. purity) at room-temperature, have already been published † ; the present paper gives the results of measurements made on the same material at different temperatures. From these measurements the coefficients of expansion of beryllium along and perpendicular to the hexagonal axis have been determined over a range of temperature extending from 20° C. to 500° C.

Experimental.

The method of procedure was the same as that adopted in the measurement of the thermal expansion of cadmium, osmium, and ruthenium ‡, all of which are elements possessing close-packed hexagonal structures.

Certain special precautions had to be taken with beryllium owing to its extreme transparency to the X-rays. It was difficult to obtain satisfactory photographs with powder specimens prepared in the usual way, and the method previously adopted with some of the other elements had to be used, namely, that of preparing powder-foil of the material by compressing fine filings between brass sheets in a rolling mill. In this way comparatively thick sheets of beryllium could be employed, and the crystals on heating for prolonged periods did not show the same tendency to grow as did those in foil prepared by rolling a sheet of cast material. To remove the effect of cold work, the powder-foil was

annealed *in vacuo* at 650° C. for $1\frac{1}{2}$ hours on its mounting on the camera before the X-ray exposure was made. With iron radiation, reflexions should be obtained from the $(10\bar{1}3)$ and $(20\bar{2}0)$ planes of beryllium, but on the photographs obtained with a copper thermo-sheet, reflexions from the planes $(10\bar{1}3)$ only were registered. Copper radiation yielded the same result, and with this radiation the lines reflected by the copper backing were stronger even than the lines from the beryllium. It was evident that, owing to the transparency of the beryllium, the radiation fell on the copper-backing with little loss of intensity, producing intense scattered radiation which obliterated some of the lines on the film. After further investigation it was found that a magnesium backing sheet was suitable at low temperatures and an aluminium sheet at higher temperatures, the reflexions from these materials being absent or well removed from the beryllium lines which had to be measured, and the scattered radiation was not of great intensity. With these backing sheets and iron radiation, doublets from the planes (1013) and $(20\bar{2}0)$ were obtained on the film at each temperature.

The thickness of the beryllium foil was 0·25 mm. The fiducial distances on the camera were adjusted so as to correct for the penetration of the specimen.

Two series of photographs were taken at various temperatures from room-temperature up to 550° C., one series was obtained with iron radiation and the other with cobalt radiation. Somewhat long exposures, about 2 hours, were necessary to obtain reflexions of sufficient intensity from the (2020) planes with iron radiation. With cobalt radiation an exposure of $1\frac{1}{2}$ hours sufficed, but from room-temperature up to 200° C. only lines from the (0004) planes were obtained on the film with this radiation ; at 200° C. lines from the (2021) planes appeared. These, together with the lines from the (0004) planes, supplied sufficient data to calculate the parameters of beryllium over the range of temperature from 200° C. to 550° C.

The series of photographs obtained with iron radiation is of interest. It has already been mentioned that the Kα doublet of iron was reflected from the planes (1013) and (2020) at room-temperature. These lines remain

on the film over the whole range of temperature employed, and at about 500° C. a reflexion from the plane (11$\bar{2}$2) also appears in the photograph. At temperatures not far removed from room-temperature the α_2 line from the (20$\bar{2}$0) plane falls almost exactly on the β-line from the (0004) plane, but with increase of temperature the two lines become resolved, the α_2 line moving out more rapidly than the β-line. Since these two reflexions take place respectively at the prism face and at the basal plane of the hexagonal unit, the resolution illustrates in a novel way that the hexagonal unit expands less rapidly along than perpendicular to the axis.

Temperature Measurement.

The thermal conductivity of beryllium is small (viz., 0·16) and that of the specimen may even be smaller. The temperature of the specimen was determined by means of a calibrated thermocouple soldered to the front surface of the backing sheet on which the specimen was mounted. An electric furnace brought up against the backing sheet served to heat the specimen, and since the thickness of the specimen was 0·25 mm., an appreciable temperature gradient probably existed in the specimen, the temperature of the front being less than that of the back face immediately in contact with the backing sheet. To determine the magnitude of the difference in temperature between front and back of the specimen, a small thermocouple sheet was prepared by silver-soldering two strips of nickel and nichrome wires to a thin copper sheet. The sheet was made thin and small to reduce its thermal capacity so that it would acquire its final temperature quickly. It was bent and ground to fit closely over the surface of the specimen. This sheet was placed between the specimen and the mica sheet, which helped to insulate the specimen thermally from the camera. The remaining parts were mounted on the camera as before, the only difference between the arrangement now and that previously employed being that the specimen was now sandwiched between two sheets furnished with thermocouples which were brought to terminals outside the evacuated enclosure in which the camera was mounted. The specimen was raised to various steady temperatures and the difference in

temperature between the back and the front of the specimen as measured by the thermocouples recorded at each temperature. Consistent readings of these differences were obtained only after great care had been taken that there was good contact between the various surfaces. The differences in the temperature between back and front plotted against the temperature given by the thermocouple in the backing sheet yielded a satisfactory curve. The correction necesary at 550° C., the highest temperature reached, amounted to 13° C. Correspondingly smaller corrections were required at lower temperatures.

Results.

A large number of exposures were made at various temperatures ranging between 15° C. and 530° C. The

TABLE I.

	$K\alpha_1$.	$K\alpha_2$.	$K\beta$.
Iron	1·93208	1·93601	1·75301
Cobalt.......	1·78529	1·78919	1·61744

specimen was always irradiated *in vacuo*, and the characteristic radiations of iron and cobalt were employed. The values of the wave-lengths of the radiations used are contained in Table I.

The films taken with iron radiation yielded the same parameter values within experimental error as did those taken at the same temperature with cobalt radiation. The results were plotted against the temperature and smooth curves were drawn to pass through the experimental points or as close as possible to them. From these curves values of the parameters were taken at temperature intervals of 50° C.—rather more frequently than this at the lower temperatures—from 20° C. to 550° C. These are contained in Table II.

Both the base side and the height of the hexagonal unit increase as the temperature is raised, but the former

increases more rapidly than the latter. From the parameter values the mean coefficient of expansion was calculated by the aid of the formula

$$\alpha_{t_2, t_1} = \frac{x_{t_2} - x_{t_1}}{(t_2 - t_1) \cdot x_{20}},$$

TABLE II.

Parameters of Beryllium at Different Temperatures.

| Temperature.	Base side (a).	Axial ratio (c).	Height (ac).	Atomic volume $(\sqrt{3} \cdot a^3 c/4)$.
20°	$2 \cdot 2813_4$ Å.	$1 \cdot 5681$	$3 \cdot 5773_2$ Å.	$8 \cdot 0619_0$ Å³.
50	$2 \cdot 2822_4$	$1 \cdot 5679_5$	$3 \cdot 5784_8$	$8 \cdot 0711_4$
80	$2 \cdot 2832_2$	$1 \cdot 5678$	$2 \cdot 5797_0$	$8 \cdot 0803_9$
100	$2 \cdot 2839_2$	$1 \cdot 5677$	$3 \cdot 5805_1$	$8 \cdot 0869_4$
150	$2 \cdot 2855_6$	$1 \cdot 5675$	$3 \cdot 5826_9$	$8 \cdot 1034_3$
200	$2 \cdot 2873_8$	$1 \cdot 5672$	$3 \cdot 5847_3$	$8 \cdot 1208_5$
250	$2 \cdot 2891_1$	$1 \cdot 5669$	$3 \cdot 5869_5$	$8 \cdot 1390_2$
300	$2 \cdot 2911_7$	$1 \cdot 5665_5$	$3 \cdot 5892_5$	$8 \cdot 1582_4$
350	$2 \cdot 2932_1$	$1 \cdot 5662$	$3 \cdot 5916_4$	$8 \cdot 1782_6$
400	$2 \cdot 2954_2$	$1 \cdot 5658$	$3 \cdot 5941_2$	$8 \cdot 1993_6$
450	$2 \cdot 2976_5$	$1 \cdot 5654$	$3 \cdot 5967_2$	$8 \cdot 2214_6$
500	$2 \cdot 3001_0$	$1 \cdot 5649$	$3 \cdot 5994_5$	$8 \cdot 2447_8$
550	$2 \cdot 3025_6$	$1 \cdot 5645$	$3 \cdot 6023_5$	$8 \cdot 2692_5$

TABLE III.

Temperature. ° C.	Mean thermal coefficient of expansion of beryllium ($\times 10^6$).			
	Perpendicular to axis $\alpha_\perp$.	Parallel to axis $\alpha_\parallel$.	(Vol. coef.)/3 $\{$ mean linear $\}$.	$(2\alpha_\perp + \alpha_\parallel)/3$.
0	$(13 \cdot 2)^*$	$(10 \cdot 8)$	$(12 \cdot 1)$	$(12 \cdot 4)$
50	$13 \cdot 7$	$11 \cdot 1$	$12 \cdot 7$	$12 \cdot 8$
100	$14 \cdot 4$	$11 \cdot 5$	$13 \cdot 3$	$13 \cdot 4$
150	$15 \cdot 1$	$11 \cdot 8$	$14 \cdot 0$	$14 \cdot 0$
200	$15 \cdot 9$	$12 \cdot 2$	$14 \cdot 7$	$14 \cdot 7$
250	$16 \cdot 7$	$12 \cdot 6$	$15 \cdot 5$	$15 \cdot 3$
300	$17 \cdot 6$	$13 \cdot 1$	$16 \cdot 2$	$16 \cdot 1$
350	$18 \cdot 6$	$13 \cdot 6$	$17 \cdot 0$	$16 \cdot 9$
400	$19 \cdot 5_5$	$14 \cdot 2$	$17 \cdot 9$	$17 \cdot 8$
450	$20 \cdot 5$	$15 \cdot 0$	$18 \cdot 8$	$18 \cdot 7$
500	$21 \cdot 5$	$15 \cdot 8$	$19 \cdot 8$	$19 \cdot 6$

* Extrapolated values.

the temperature interval $(t_2 - t_1)$ being 100° C., except at the lowest temperatures.

The calculated values of the mean thermal coefficients along and perpendicular to the hexagonal axis are given in Table III.

This table contains also the mean linear coefficient of expansion calculated from the atomic volume, and in the last column of the table are inserted the values of $(2\alpha_\perp + \alpha_{||})/3$. These will be observed to agree very well with the figures in the fourth column, thus indicating that the curves have been fairly accurately drawn. No abnormality of any kind in the expansion
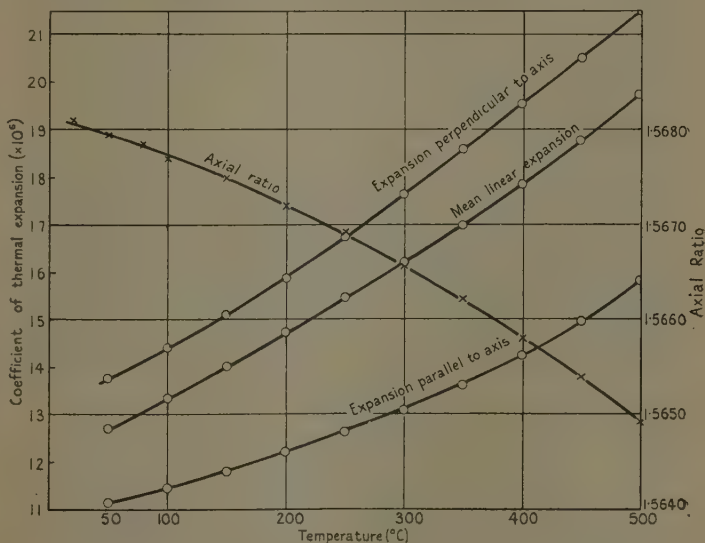
of the material was observed within the range of temperature investigated. In the figure are shown the relations between the various mean coefficients of expansion and the temperature. The variation of axial ratio with temperature is also shown in this diagram.

As far as could be ascertained the only work done on the thermal expansion of beryllium is that by Hidnert and Sweeney * ; they determined the mean linear coefficient of thermal expansion. The only values of the coefficient of expansion of beryllium along and perpen-

* Sci. Papers Bur. Stds. no. 565, xxii. p. 533 (1927).

dicular to the axis are those quoted in a paper recently published from this laboratory *. The values of Hidnert and Sweeney are included in Table IV. together with those now found.

Hidnert and Sweeney made their measurements on a cast rod of beryllium containing 98·9 per cent. beryllium.

TABLE IV.

Range of temperature.	Mean linear coefficient of expansion ($\times 10^6$).	
	Present values.	Hidnert and Sweeney.
20°–100° C.	12·$_9$	12·3
20°–200° C.	13·$_5$	13·3
20°–300° C.	14·$_2$	14·0
20°–400° C.	14·$_9$	14·8
20°–500° C.	15·$_7$	15·5

30 cm. long and 1 cm. in diameter. The purity of the material used in the present work was 99·8 per cent. The agreement between the figures in Table IV. is good in the middle of the temperature range, but deviations between the two sets of values are observed at each end of the temperature range. The present expansion curves are not so securely fixed at the extreme temperatures as

TABLE V.

Parameter of Beryllium at 20° C.

Base side.	Axial ratio.	Reference.
2·2812$_6$	1·5684$_3$	*Z. f. Krist.* xci. p. 70 (1935).
2·2811$_1$	1·5681$_3$	*Phil. Mag.* xx. p. 1155 (1935).
2·2813$_4$	1·5680$_8$	Present work.
2·2812$_4$	1·5682$_1$	Mean values.

they are at intermediate temperatures, and this probably accounts for the greater deviations observed at the end points.

The values of the parameters of beryllium at 20° C. obtained in three different investigations carried out by workers in this laboratory are collected in Table V.

* Owen, Pickup, and Roberts, *Zeit. f. Krist.* xci. p. 70 (1935).

Summary.

The thermal expansion of beryllium, the purity of which was 99·8 per cent., was measured by the X-ray method along and perpendicular to the hexagonal axis over a range of temperature from 20° C. to 550° C.

The structure of beryllium remained close-packed hexagonal over the whole range of temperature investigated. The mean parameters of beryllium at 20° C. are : $a = 2·2812_4$ Å. and $c = 1·5682_1$, each to an accuracy of $\pm 0·0003$.

The thermal coefficient of expansion both along and perpendicular to the hexagonal axis increases with temperature, the coefficient parallel to the axis increasing less rapidly than that perpendicular to the axis. The axial ratio thus decreases with rise of temperature.

At 50, 100, 200, 300, 400, and 500° C., the values of $\alpha_\perp$ are 13·7, 14·4, 15·9, 17·6, $19·5_5$, and $21·5 \times 10^{-6}$, and those of $\alpha_\parallel$ are 11·1, 11·5, 12·2, 13·1, 14·2, and $15·8 \times 10^{-6}$.

In the paper are also included values of the mean linear coefficient of expansion of beryllium, and the results are compared with the only values previously published ; the two sets of values are found to be in satisfactory agreement over the greater part of the temperature range covered by the observations.

XXVI. *The Production of Piezoelectricity by Torsion.* *By* Reginald E. Gibbs, D.Sc., *and* Ling-Chao Tsien, *B.Sc.* *

[Plate I.]

Introduction.

THE first attempt to produce piezoelectricity by torsion was made in 1890 by Röntgen †, who twisted quartz crystals cut cylindrically parallel to a crystal axis. He

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† W. C. Röntgen, *Wied. Ann.* xxxix. p. 16 (1890).

was never really satisfied with his own observations, which were in disagreement with Voigt's general theory of piezoelectricity, but it fell later to Voigt * to show that Röntgen's unexpected results arose merely from slight lack of parallelism of the axis of twisting and one or other of the crystal structural axes. Voigt † dealt extensively with the general theory of twisting and bending. The present paper deals with the particular case of a right circular quartz cylinder cut parallel to and twisted about the optic axis of the specimen. Some observations upon the static production of electricity corresponding with this case have been advanced recently by Tawil ‡, who claimed to have established that the phenomenon was distinct from that of piezoelectricity, and reserved for it the name " strephoélectricité." Subsequent considerations will show that this is quite unnecessary, the usual theory affording adequate explanations of all the observations. The subject has received the attention also of Ny and Tsien §, who have studied the phenomena more extensively.

It may be well to recapitulate their main results, particularly as references to them will have to be made later. A solid cylinder under torsion develops a charge of one sign on its cylindrical surface and of the opposite sign on its end faces. Tawil records a uniform distribution for the former charge, but Ny and Tsien find the uniformity only partial, the charge density possessing cylindrical symmetry but being a minimum or zero at the central section and increasing with distance from this position. They show also that the cylindrical surface possesses a charge of only one sign.

Ny and Tsien further find that a hollow cylinder under torsion develops equal and opposite charges uniformly distributed on its outer and inner surfaces, the magnitude of the charges being greater than for a corresponding solid cylinder. In both cases the sign of a charge is correlated definitely with the sense of torsion and of the optical rotation. Both Tawil and Ny and Tsien find the magnitude of the charges produced to be proportional

* W. Voigt and V. Freedericksz, *Ann. der Phys.* xlviii. p. 145 (1915).
† W. Voigt, *Ann. der Phys.* xlviii. p. 433 (1915).
‡ E. P. Tawil, *Compt. Rend.* clxxxvii. p. 1042 (1928) ; cxcix. p. 1025 (1934) ; cc. pp. 1088 & 1306 (1935).
§ Ny Tsi-Ze, and Tsien Ling-Chao, *Compt. Rend.* cxcviii. p. 1395, cxcix. p. 1101 (1934).

to the torque, but advance rather different formulæ. Tawil requires $Q = H \cdot \dfrac{CL}{\pi(r_0{}^2 - r_i{}^2)}$, where Q = charge developed, C kg. cm. = applied couple, L cm. = length of cylinder subject to torsion, r_0, r_i cm. = outer and inner radii. Within experimental error H then has a constant value of $0 \cdot 12$ C.G.S. e.s.u. On the other hand, Ny and Tsien find that $Q = H' \cdot \dfrac{CL}{4r_0(r_0 - r_i)}$, where H' has the

Fig. 1.
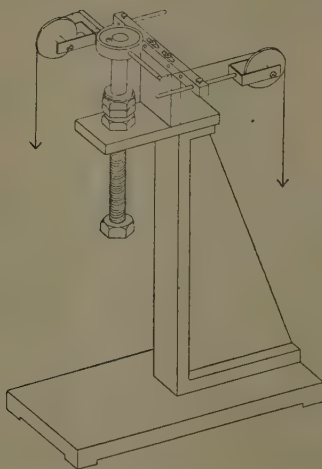
value $9 \cdot 3 \cdot 10^{-8}$ abs. c.g.s. units. Using a number of cylinders these experimenters were able to show that H' remains sensibly constant when the factor $\dfrac{L}{4r_0(r_0 - r_i)}$ ranges from $0 \cdot 79$ to $23 \cdot 3$ cm.$^{-1}$.

Static Observations and Deductions.

We decided to make some observations upon the charges produced by static torsion, and in particular to simplify their detection by the use of a Lindemann electrometer. The torsion apparatus designed for this purpose is shown in fig. 1, while fig. 2 depicts the electro-

meter circuit. After careful cleaning of the crystal, two tinfoil electrodes were affixed with a little seccotine, which adhesive was used also to attach the crystal to the annular rings through which the couple was applied. The electrometer proved quite sensitive and, with the magnification in use, gave nearly a full-scale deflexion for a couple of the order of 10 gm. metres, without in any way extending the sensitivity of the instrument. Precautions were taken to enclose the cylinder in an external metal shield, to render possible an approximate allowance for stray capacity.   With such an allowance the charges developed upon the outer and inner electrodes always proved nearly equal.

Fig. 2.
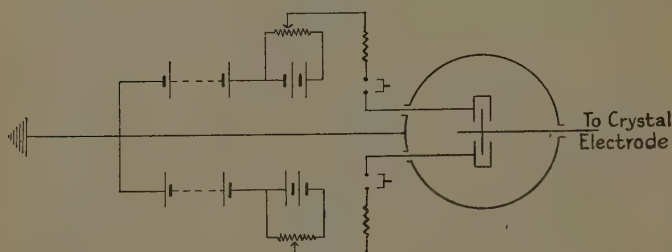
The polarization produced by torsion can easily be obtained theoretically by a suitable reduction of Voigt's general equations, which, using the accepted notations, are

$$-p_x = \delta_{11}(X_x - Y_y) + \delta_{14}Z_y,$$
$$-p_y = -\delta_{14}Z_x - 2\delta_{11}X_y,$$
$$-p_z = 0 ;$$

p_x, p_y, p_z are the polarizations along the electric, third, and optic axes respectively, $X_x \ldots$, $X_y \ldots$ etc. the stresses, and δ_{11}, δ_{14} the piezoelectric moduli. For an elementary volume in a cylinder under torsion about the z axis the stresses are $Z_x = t \cos\theta$, $Z_y = t \sin\theta$, $X_x = Y_y = Z_z = X_z = $ etc. $= 0$, where θ is the angular separation of the radius through the volume and the x axis, and t is the shearing force perpendicular to this radius and to the z axis. Voigt's equations thus become $p_x = -\delta_{14}\, t \cos\theta$

$p_y = \delta_{14}\,t\sin\theta$, $p_z = 0$, so that the polarization p is radial and of magnitude $\delta_{14}t$ per unit area. It appears at once therefore that the charge density should be uniform over a cylindrical surface and of one sign only. If a torque T is applied to the ends of a cylinder, of which the length is l and the inner and outer radii r_i r_0, the shearing force t at any position, distant r from the axis, is given by the relation

$$t = \frac{2r\mathrm{T}}{\pi(r_0{}^4 - r_i{}^4)}.$$

The total charge on the outer surface Q_{r_0} is

$$\delta_{14}\cdot\frac{4l\mathrm{T}r_0{}^2}{(r_0{}^4 - r_i{}^4)},$$

and that on the inner surface $-\mathrm{Q}_{r_i}$ is

$$-\delta_{14}\cdot\frac{4l\mathrm{T}r_i{}^2}{(r_0{}^4 - r_i{}^4)}.$$

Thus torsion necessarily involves a radial variation of shear and a corresponding radial variation of charge proportional to r^2, which necessitates the existence of a volume charge of amount $\dfrac{\partial\mathrm{Q}_r}{\partial r}\,.\,dr$. As the total charges generated must necessarily add up to zero, the values are connected as follows:

$$\mathrm{Q}_{r_0} = \mathrm{Q}_{r_i} + \int_{r_i}^{r_0}\frac{\partial\mathrm{Q}_r}{\partial r}\,.\,dr.$$

Further consideration was given to demonstrating this inequality of Q_{r_0} and Q_{r_i}, but all experiments pointed to the equality of the charges measured—in fact, no experiment which would disclose such an inequality could be devised with the cylinder. A consideration of the effective disposition of the electrodes, shields, etc. (assuming always an infinite cylinder, *i. e.*, neglecting end effects) led to the realization that the electrode charges Q_0 and $-\mathrm{Q}_i$ should themselves be equal though not equal to either surface charge. Assuming the inner and outer electrodes form a complete shield the total induction from the cylindrical surfaces would be

$$\mathrm{N}_0 + \mathrm{N}_i = 4\pi\left(\mathrm{Q}_{r_0} - \mathrm{Q}_{r_i} - \int_{r_i}^{r_0}\frac{\partial\mathrm{Q}_r}{\partial r}\,.\,dr\right) = 0,$$

where N_0, N_i are the outward normal inductions. Thus, finally, $N_0 = -N_i$ and $Q_0 = Q_i = Q$.

The inequality of Q_{r_0} and Q_{r_i} was substantiated by experimental evidence of the volume charge. This was not possible with the cylinder, but, as such a charge accompanies the spacial variations of shear, a more suitable quartz cut could be chosen to demonstrate its existence. The slab shown in fig. 3 was cut accurately perpendicular to the optic axis and subjected to tension along a line parallel to the third direction. It might have been preferable to cut the slab into a shape more consistent with nearly stress-free edges, but to avoid this the edge was covered completely with an earthed tinfoil strip. The crystal was held by toolmakers clamps,

Fig. 3.
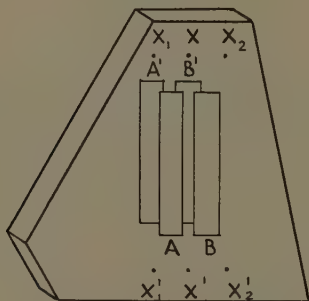
between the jaws of which, on each side, were placed a small short brass cylinder and a thin rubber pad. In this way tension could be applied between two points such as XX'. Four tinfoil electrodes were affixed to the flat surfaces as shown, and the tension applied between (I) XX' or (II) X_1X_1' or (III) X_2X_2'. The electrodes were connected, (a) separately at first, and afterwards in pairs (b) AA' and BB', or (c) AB and A'B', with the electrometer, and in all cases the indications were consistent with expected results. Arrangement (I a) gave A and A' say positive and B, B' negative, all to an equal extent, (2 a) gave A, A' negative and B, B' less negative, whilst (3 a) gave A, A' positive and B, B' more positive. Arrangements (I b, II b, III b) gave corresponding results, whilst (I c) resulted in no deflexion. Such results could arise

only from stress variation and volume charge. It was subsequently found that Giebe and Scheibe * had demonstrated the existence of a volume charge in the case of oscillations by their method of glow discharge, *e. g.*, for the case of a rod cut along the electric axis.

Reverting to the case of a cylinder, fig. 4, which represents a half section of the cylinder and its electrodes, illustrates the effective disposition of the charges, and is helpful in discovering the relationship between Q, Q_{r_0}, and Q_{r_i}. C is any internal coaxial cylindrical surface of radius r, at which position a polarization Q_r is produced,

Fig. 4.
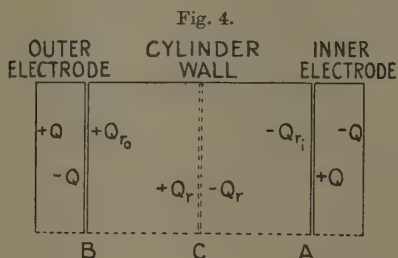
and the electric force at this surface due to the charge $-Q_{r_i}$ and the volume charge between A and C is

$$-\frac{2}{\mathrm{K}rl}\left(Q_{r_i}+\int_{r_i}^{r_0}\frac{\partial Q_r}{\partial r}\cdot dr\right)=-\frac{2Q_r}{\mathrm{K}rl}$$
$$=-\frac{8r\delta_{14}\mathrm{T}}{\mathrm{K}(r_0{}^4-r_i{}^4)}=kr,$$

where K is the dielectric constant.

The potential difference between A and B is

$$-k\int_{r_i}^{r_0}r\,dr=\frac{Q_{r_0}-Q_{r_i}}{\mathrm{K}l},$$

and, as the capacity of the cylinder is

$$\frac{\mathrm{K}l}{2\log r_0/r_i},$$

$$Q=\frac{Q_{r_0}-Q_{r_i}}{2\log r_0/r_i}=\frac{2\,\delta_{14}l\mathrm{T}}{(r_0{}^2+r_i{}^2)\log r_0/r_i}.$$

* E. Giebe and A. Scheibe, *Zeits. f. Phys.* xlvi. p. 607 (1928).

Langevin * has also been led to disclaim any necessity for strephoélectricité, and, in fact, arrived at the same formula.

This formula may now be compared with those advanced by other experimenters, who, one must assume, have measured Q, and not Q_{r_0} or Q_{r_i}, by stating what terms their " constants " H and H′ must be made to include ; such a method permits a measure of comparison between

Fig. 5.
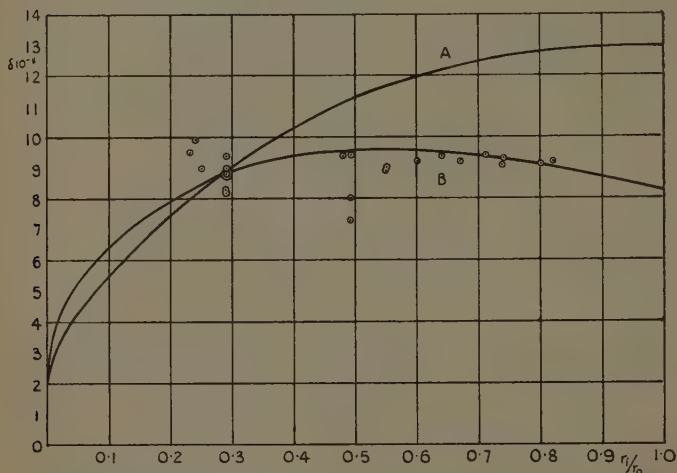
their practical results and the theoretical formula.   Tawil's equation would require H to embrace the terms

$$\left[\frac{2\,\delta_{14}(1-r_i/r_0)}{(1+r_i^2/r_0^2)\log r_0/r_i} \right] \pi(1+r_i/r_0) = \pi(1+r_i/r_0)\mathrm{F},$$

whilst Ny and Tsien's H′ would have to be 4F.   The values of H and H′ for various values of r_i/r_0 are plotted in fig. 5, in which neither curve exhibits constancy.   The two equations are not mutually consistent, and one is led to select as the better that of Ny and Tsien †.   Tawil's " constant " (curve A) is subject to a continuous variation,

* P. Langevin and J. Solomon, *Compt. Rend.* cc. p. 1257 (1935).
† Ny, Tsi-Ze, and Tsien Ling-Chao, *Compt. Rend.* cc. p. 732 (1935).

but the curve (B) can be considered as approximately constant over the experimental range, and, in fact, from Ny and Tsien's results it is not possible to distinguish with certainty between their formula and that suggested here, assuming that the value of δ_{14} is so chosen as to raise the general level of the curve to a suitable position. Such a value is about $2 \cdot 07 \cdot 10^{-8}$, which compares rather poorly with the value usually quoted, viz., $1 \cdot 45 \cdot 10^{-8}$. The latter figure originated from the work of Rieke and Voigt * in 1892, and has never received confirmation ; in the next year Pockels †, in a long and apparently accurate research, concluded that the value should be $1 \cdot 925 \cdot 10^{-8}$, whilst many years later Voigt by a comparison of the effects of δ_{11} and δ_{14}, computed the value of the latter to be $2 \cdot 24 \cdot 10^{-8}$. There seems therefore to be nothing against the value suggested—in fact, an acceptance of Ny and Tsien's values and of the present formula would demand this value for δ_{14}.

To test more effectively the validity of the formula would require an extension of the measurements ‡ to cylinders of smaller axial cavity, *i. e.*, approaching solid cylinders. Some support for the marked falling off shown by the formula at low values of r_i/r_0 is offered by the comparatively small effect obtained experimentally with solid cylinders. These can be regarded as merely the limiting case of the hollow variety, in which r_i/r_0 becomes zero, so that any measurable charge must arise from end effects for which no allowance can be made in the calculation beyond a realization that the value of the constant would apparently be increased.

Torsional Oscillations.

Hund §, who employed several circuits and a number of electrode mountings, attributed the difficulty which he experienced, of putting the cylinders into oscillation other than by the use of fairly regenerative circuits, to the small value of δ_{14}. It appears that such a difficulty is more likely to arise partly from the use of solid cylinders and

* E. Rieke and W. Voigt, *Wied. Phys. u. Chem.* xlv. p. 523 (1892).

† F. Pockels, *Abhandl. Kön. Ges. Gött.* xxxix. p. 206 (1893). See also H. Osterberg and J. W. Cookson, Rev. Sc. Inst. vi. p. 349 (1935).

‡ In answer to a private communication of December 1934, detailing the above formula, we understand that Ny would apply this test by extending the measurements to cover the lower range.

§ A. Hund and R. B. Wright, J. Res. Bur. Stan. iv. p. 383 (1930).

partly from the complicated electrode distribution which he employed sometimes. Hund stated that the most successful mounting for the production of torsional oscillations was one electrode covering the cylindrical surface and two others, connected together, covering the ends, *i. e.*, his mounting B, to which C was an approximation. This agrees with the theory in corresponding exactly with the positions where the opposite charges would be located ; the end charges are really part of the volume charge. The other mountings, A and D to G, could not be expected to be suitable for the excitation of torsional oscillations, as, except for chance inequalities,

Fig. 6.
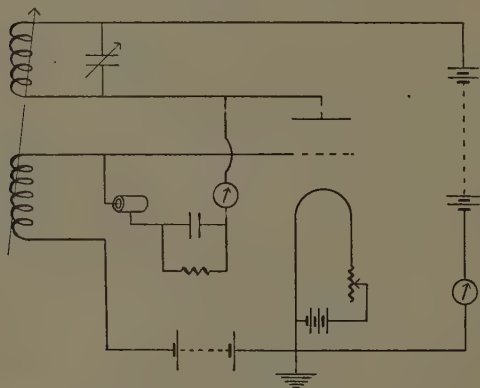
the effects of the electrodes would all appear to neutralize. Ny and Tsien * obtained three modes of oscillation of hollow cylinders including the torsional mode, and were able to find experimental constants to insert in frequency formulæ.

A short investigation of torsional excitation was made, using, as means of detection, Kundt's dust method, Giebe and Scheibe's glow discharge method and polarized light. A quick yet useful survey of the modes of vibration could be made by exploring the surface very lightly with the end of a wire ; the segments and nodal positions disclosed themselves quite effectively. The circuit (fig. 6)

* Ny, Tsi-Ze, and Tsien Linʒ Chao, *Compt. Rend.* cc. p. 565 (1935).

finally employed was a slight modification of one of the normal types. In some cases the oscillations generated were so vigorous that high temperatures, melted electrodes, and cracked specimens resulted very quickly, particularly in the vacuum discharge method, in which a destructive direct current discharge was prone to develop. This was subsequently avoided by the introduction of the extra 2 microfarad condenser and 2 megohm leak. One of the cracked specimens is reproduced in fig. 7 (Pl. I.), which shows clearly the spiral crack formation; such cracks made on an average an angle of $48°$ with the horizontal. The table records in k.c. some of the resonant frequencies obtained. One method of separating frequencies was to follow their change or constancy as the cylinder was ground progressively to shorter lengths,

Cylinder........	I.	II_1.	II_2.	II_3.	II_4.	II_5.	III.	IV
l cm.	4·94	3·25	3·20	1·67	1·57	1·535	2·71	0·97
r_0 cm.	0·885	0·785	0·785	0·785	0·785	0·785	0·870	1·530
r_i cm.	0·570	0·525	0·525	0·525	0·525	0·537	0·270	0·500
Theoretical	44·3	67·3	68·4	131·0	139·5	142·5	80·8	..
Experimental ...	44·3	67·5	68·8	132·5	131·5	142·5	81·3	..
Theoretical	362	..	401	401	401	398	..	259
Experimental ...	368	..	408	408	395	399	..	254

such as, for example, in the case of cylinders II_1 to II_5. A case of particular interest is that of cylinder I, for which the torsional frequency was sufficiently far removed from those of other modes as to preclude any doubt of its origin. The polarized light patterns were obtained sometimes by the use of a mercury arc and a Wratten violet filter, in which case, by appropriate setting of the nicols, the pattern appeared in colours, or with a sodium discharge-tube and crossed nicols, which gave greater contrast. The patterns, frequently obtained, were of the six-spot type shown in fig. 8 (*a*) (Pl. I.); it was not possible to decide from which mode of vibration the pattern corresponding to fig. 8 (*b*) (Pl. I.) originated. In conclusion, the possibility of the excitation of torsional oscillations cannot be in doubt in view of the agreement existing between the results of Hund, of Ny and Tsien, and of those recorded here.

Acknowledgments.

Summary.

The production of piezoelectricity by torsion is considered for the case of right circular cylinders of quartz cut with their axes parallel to the optic axis. The experimental observations of other experimenters are shown to agree with the theoretical formula deduced. The Lindemann electrometer was shown to be suitable and very convenient for the study of piezoelectricity, and was used to demonstrate experimentally the static development of volume charges. Torsional oscillations have been produced in both hollow and solid cylinders, and were studied by the glow discharge, dust, and polarized light methods.

XXVII. *Specific Thermodynamic Properties of Aqueous Solutions of Uni-univalent Electrolytes.* By E. A. GUGGENHEIM, *M.A.* *

IN two previous papers [1], [2] † a theory was described which enables us to compute for any aqueous solution of electrolytes of total ionic strength not exceeding 0·1 the osmotic coefficient of the solution and the activity coefficient of each of the electrolytes present in the solution. The formulæ of this theory contain only one adjustable parameter corresponding to each electrolyte. Each such parameter is most conveniently determined by freezing-point or electromotive force measurements on solutions containing only the one electrolyte. It has been shown that all the most reliable experimental data (with the single exception of the ammonium salts [3] which apparently do not even obey the usual limiting

law of Debye and Hückel for high dilutions) are in good agreement with our formulæ. In the present paper these formulæ will be applied to new experimental data.

All the new data are for solutions of single uni-univalent electrolytes. The osmotic coefficient g at $0°$ C. for a solution of the single uni-univalent electrolyte RX at the concentration C is given by

$$1-g = 0\cdot374\,C^{\frac{1}{2}}\,\sigma(C^{\frac{1}{2}}) - \frac{2\cdot30}{2}\,\lambda_{R,\,X}\,C, \quad . \quad . \quad (1)$$

where σ is the function defined by

$$\sigma(x) \equiv 3\left\{\frac{1}{3} - \frac{2}{4}x + \frac{3}{5}x^2 - \frac{4}{6}x^3 + \frac{5}{7}x^4 \ldots\right\}. \quad . \quad (2)$$

A table of values of $\sigma(C^{\frac{1}{2}})$ is included in the previous paper [2]. $\lambda_{R,\,X}$ is a constant, there being one such parameter for each single electrolyte. The same parameters occur in the formulæ for solutions containing several electrolytes. The corresponding formula for the mean activity coefficient $f_{R,\,X}$ of the single electrolyte R, X at the concentration C is given at $20°$ C. by

$$-\log_{10}f_{R,\,X} = 0\cdot500\,\frac{C^{\frac{1}{2}}}{1+C^{\frac{1}{2}}} - \lambda_{R,\,X}\,C. \quad . \quad . \quad (3)$$

Since a small alteration in this coefficient $0\cdot500$ can be compensated by an alteration in the value assigned to $\lambda_{R,\,X}$, we may safely use the coefficient $0\cdot500$ for any temperature between $15°$ C. and $25°$ C. At $0°$ C. the coefficient should be $0\cdot486$.

In Tables I. to XII. are given the results of the computations for the freezing-point data of Scatchard, Prentiss, and Jones [4], [5] for the chlorates, perchlorates, nitrates, formates, and acetates of lithium, sodium, and potassium. In each table the first column gives m the molality : the second column gives $C^{\frac{1}{2}}$ the square root of the concentration ; the third column gives the value of $1-g$ computed according to the formula at the head of the table ; the fourth column gives the published experimental value of $1-\phi$, where ϕ is the osmotic coefficient on the molality scale ; the fifth column gives the corresponding experimental value of $1-g$, where g is the rational osmotic coefficient ; the sixth column gives the difference between values computed and observed

TABLE I.

Freezing-point Data of Scatchard, Prentiss,
and Jones on LiClO₃.

$$1-g=0.374\ C^{\frac{1}{2}}\sigma(C^{\frac{1}{2}})-0.280\ C.$$

$m.$	$C^{\frac{1}{2}}.$	$1-g_{\text{theor.}}$	$1-\phi_{\text{exp.}}$	$1-g_{\text{exp.}}$	$\theta_{\text{exp.}}-\theta_{\text{theor.}}$
·000627	·0250	·0088	·0300	·0300	− ·00004
·000753	·0274	·0096	− ·0006	− ·0006	+ ·00002
·001109	·0333	·0116	·0053	·0053	+ ·00003
·001396	·0374	·0129	·0072	·0072	+ ·00003
·002100	·0458	·0154	·0274	·0274	− ·00009
·002192	·0468	·0157	·0202	·0202	− ·00003
·002983	·0546	·0181	·0185	·0184	·00000
·003849	·0620	·0201	·0261	·0260	− ·00008
·005650	·0752	·0237	·0236	·0235	·00000
·009870	·0993	·0294	·0282	·0280	+ ·00005
·013646	·1168	·0332	·0328	·0326	+ ·00003
·018748	·1369	·0370	·0353	·0351	+ ·00013
·021459	·1465	·0386	·0383	·0380	+ ·00005
·029040	·1704	·0422	·0403	·0398	+ ·00025
·038551	·1963	·0451	·0439	·0433	+ ·00025
·057068	·2389	·0486	·0472	·0463	+ ·00048
·086081	·2934	·0501	·0513	·0498	+ ·00009
·11738	·3427	·0490	·0522	·0502	− ·00051

TABLE II.

Freezing-point Data of Scatchard, Prentiss,
and Jones on NaClO₃.

$$1-g=0.374\ C^{\frac{1}{2}}\sigma(C^{\frac{1}{2}})-0.040\ C.$$

$m.$	$C^{\frac{1}{2}}.$	$1-g_{\text{theor.}}$	$1-\phi_{\text{exp.}}$	$1-g_{\text{exp.}}$	$\theta_{\text{exp.}}-\theta_{\text{theor.}}$
·000889	·0298	·0107	·0162	·0162	− ·00002
·001029	·0321	·0114	·0193	·0193	− ·00003
·001825	·0427	·0148	·0179	·0179	− ·00002
·003726	·0610	·0208	·0192	·0191	+ ·00002
·005256	·0725	·0242	·0246	·0245	− ·00001
·011793	·1086	·0343	·0333	·0331	+ ·00005
·015730	·1254	·0387	·0381	·0378	+ ·00005
·024412	·1562	·0460	·0443	·0439	+ ·00018
·034813	·1865	·0525	·0537	·0531	− ·00008
·046961	·2167	·0585	·0595	·0588	− ·00005
·054084	·2326	·0612	·0604	·0595	+ ·00033
·073388	·2709	·0676	·0691	·0679	− ·00008
·089482	·2992	·0717	·0728	·0714	+ ·00010

for the freezing-point lowering θ. The correction from ϕ to g is made by using the formula

$$g = \phi(1+0\cdot018m) \quad . \quad . \quad . \quad . \quad (4)$$

valid in dilute aqueous solution for any symmetrical electrolyte.

TABLE III.

Freezing-point Data of Scatchard, Prentiss, and Jones on $KClO_3$.

$$1-g = 0\cdot374 \; C^{\frac{1}{2}}\sigma(C^{\frac{1}{2}}) + 0\cdot165 \; C.$$

m.	$C^{\frac{1}{2}}$.	$1-g_{\text{theor.}}$	$1-\phi_{\text{exp.}}$	$1-g_{\text{exp.}}$	$\theta_{\text{exp.}}-\theta_{\text{theor.}}$
·000485	·0220	·0081	·0623	·0623	$-$·00010
·000581	·0241	·0088	·0134	·0134	$-$·00001
·001281	·0358	·0129	·0105	·0105	$+$·00001
·001627	·0403	·0146	·0208	·0208	$-$·00004
·002998	·0548	·0195	·0128	·0127	$+$·00008
·004560	·0675	·0237	·0233	·0232	$+$·00001
·005520	·0743	·0259	·0235	·0234	$+$·00005
·010584	·1029	·0249	·0315	·0313	$-$·00025
·012380	·1113	·0375	·0318	·0316	$+$·00027
·012469	·1117	·0377	·0319	·0317	$+$·00028
·017878	·1337	·0442	·0413	·0410	$+$·00021
·029782	·1725	·0556	·0527	·0522	$+$·00038
·034003	·1844	·0589	·0637	·0632	$-$·00054
·036929	·1922	·0610	·0656	·0650	$-$·00055
·037653	·1940	·0617	·0591	·0585	$+$·00045
·039814	·1996	·0632	·0605	·0599	$+$·00049
·043067	·2075	·0654	·0637	·0630	$+$·00038
·055946	·2365	·0733	·0727	·0718	$+$·00031
·062245	·2495	·0769	·0782	·0772	$-$·00007
·079393	·2817	·0854	·0863	·0850	$+$·00012
·10623	·3260	·0969	·0990	·0973	$-$·00016

An examination of the last columns of the tables shows that deviations of 2×10^{-4} °C. between the computed and observed freezing-point are fairly common, but that there are few deviations as high as 4×10^{-4} °C. In a decimolar solution of a uni-univalent electrolyte a deviation of 4×10^{-4} °C. in the freezing-point corresponds to a deviation of about 1·6 per cent. in $1-g$, of 4 per cent. in $\log_e f$. of 1·6 per cent. in $\log_{10} f$, and of 0·4 per cent. in f. This degree of accuracy in the values of f is adequate for almost all practical needs. It is difficult to judge whether the

TABLE IV.

Freezing-point Data of Scatchard, Prentiss, and Jones on $LiClO_4$.

$$1-g = 0.374\ C^{\frac{1}{2}}\sigma(C^{\frac{1}{2}}) - 0.380\ C.$$

$m.$	$C^{\frac{1}{2}}.$	$1-g_{\text{theor.}}$	$1-\phi_{\text{exp.}}$	$1-g_{\text{exp.}}$	$\theta_{\text{exp.}}-\theta_{\text{theor.}}$
·000616	·0248	·0088	—·0056	—·0056	+·00003
·001014	·0318	·0110	·0101	·0101	·00000
·001941	·0441	·0148	·0226	·0226	—·00005
·002265	·0476	·0157	·0222	·0222	—·00005
·003267	·0572	·0185	·0140	·0140	+·00005
·007050	·0840	·0252	·0244	·0243	+·00002
·011698	·1082	·0302	·0275	·0273	+·00012
·014363	·1198	·0324	·0292	·0290	+·00018
·023604	·1536	·0373	·0359	·0355	+·00015
·028497	·1688	·0386	·0368	·0363	+·00024
·040513	·2012	·0416	·0396	·0390	+·00038
·056796	·2383	·0430	·0431	·0422	+·00017
·078687	·2805	·0423	·0437	·0423	·0000
·10871	·3297	·0387	·0439	·0420	—·0013

TABLE V.

Freezing-point Data of Scatchard, Prentiss, and Jones on $NaClO_4$.

$$1-g = 0.374\ C^{\frac{1}{2}}\sigma(C^{\frac{1}{2}}) - 0.075\ C.$$

$m.$	$C^{\frac{1}{2}}.$	$1-g_{\text{theor.}}$	$1-\phi_{\text{exp.}}$	$1-g_{\text{exp.}}$	$\theta_{\text{exp.}}-\theta_{\text{theor.}}$
·001049	·0324	·0115	·0136	·0136	—·00001
·001339	·0366	·0129	·0132	·0132	·00000
·002648	·0515	·0177	·0183	·0183	—·00001
·003335	·0577	·0197	·0228	·0228	—·00004
·007050	·0840	·0274	·0262	·0261	+·00003
·010984	·1048	·0330	·0334	·0332	—·00001
·012620	·1123	·0349	·0343	·0341	+·00004
·023918	·1547	·0448	·0431	·0427	+·00018
·030269	·1740	·0488	·0479	·0474	+·00015
·036284	·1904	·0520	·0537	·0531	—·00014
·061426	·2479	·0617	·0633	·0623	—·00013
·078021	·2793	·0662	·0670	·0657	+·00014
·093410	·3056	·0692	·0698	·0683	+·00031
·11620	·3409	·0732	·0762	·0743	—·00046

TABLE VI.

Freezing-point Data of Scatchard, Prentiss, and Jones on $KClO_4$.

$$1-g=0.374\ C^{\frac{1}{2}}\sigma(C^{\frac{1}{2}})+0.50\ C.$$

$m.$	$C^{\frac{1}{2}}.$	$1-g_{\text{theor.}}$	$1-\phi_{\text{exp.}}$	$1-g_{\text{exp.}}$	$\theta_{\text{exp.}}-\theta_{\text{theor.}}$
·001776	·0422	·0157	·0333	·0333	— ·00011
·003612	·0601	·0224	·0195	·0194	+ ·00004
·004936	·0703	·0263	·0377	·0376	— ·00020
·006690	·0818	·0306	·0262	·0261	+ ·00011
·008928	·0945	·0354	·0411	·0410	— ·00019
·009872	·0994	·0372	·0435	·0433	— ·00022
·012492	·1118	·0419	·0414	·0412	+ ·00003
·016215	·1273	·0479	·0521	·0519	— ·00024
·022542	·1501	·0568	·0577	·0575	— ·00006
·022927	·1514	·0572	·0575	·0572	·00000
·029631	·1721	·0655	·0676	·0671	— ·00017
·030369	·1743	·0663	·0659	·0654	+ ·00010
·044821	·2117	·0816	·0816	·0809	+ ·00011
·045841	·2141	·0827	·0823	·0816	+ ·00018
·048335	·2199	·0851	·0892	·0884	— ·00058

TABLE VII.

Freezing-point Data of Scatchard, Prentiss, and Jones on $LiNO_3$.

$$1-g=0.374\ C^{\frac{1}{2}}\sigma(C^{\frac{1}{2}})-0.260\ C.$$

$m.$	$C^{\frac{1}{2}}.$	$1-g_{\text{theor.}}$	$1-\phi_{\text{exp.}}$	$1-g_{\text{exp.}}$	$\theta_{\text{exp.}}-\theta_{\text{theor.}}$
·000632	·0251	·0089	·0207	·0207	— ·00003
·001200	·0346	·0120	·0267	·0267	— ·00007
·002669	·0517	·0172	·0230	·0230	— ·00006
·003253	·0570	·0188	·0230	·0229	— ·00005
·007210	·0849	·0262	·0251	·0250	+ ·00003
·007473	·0864	·0266	·0266	·0265	·00000
·013703	·1170	·0335	·0318	·0316	+ ·00010
·021140	·1454	·0389	·0377	·0374	+ ·00012
·037397	·1934	·0457	·0450	·0444	+ ·00018
·048107	·2191	·0472	·0488	·0480	— ·00014
·062754	·2505	·0505	·0500	·0490	+ ·00035
·093540	·3059	·0521	·0545	·0530	— ·00031

Table VIII.

Freezing-point Data of Scatchard, Prentiss, and Jones on $NaNO_3$.

$$1-g = 0.374 \ C^{\frac{1}{2}}\sigma(C^{\frac{1}{2}}).$$

m.	$C^{\frac{1}{2}}$.	$1-g_{\text{theor.}}$	$1-g_{\text{exp.}}$	$1-g_{\text{exp.}}$	$\theta_{\text{exp.}}-\theta_{\text{theor.}}$
·000803	·0283	·0102	·0248	·0248	$-$·00004
·000985	·0314	·0112	·0165	·0165	$-$·00002
·002096	·0458	·0160	·0217	·0217	$-$·00004
·003101	·0557	·0192	·0220	·0220	$-$·00003
·006389	·0799	·0267	·0262	·0261	$+$·00001
·010875	·1043	·0336	·0315	·0313	$+$·00009
·017605	·1327	·0411	·0394	·0391	$+$·00013
·021100	·1453	·0443	·0428	·0425	$+$·00014
·036711	·1916	·0550	·0539	·0533	$+$·00023
·055233	·2350	·0639	·0637	·0628	$+$·00023
·073695	·2715	·0705	·0718	·0706	$-$·00003
·093962	·3066	·0764	·0788	·0773	$-$·00032

Table IX.

Freezing-point Data of Scatchard, Prentiss, and Jones on KNO_3.

$$1-g = 0.374 \ C^{\frac{1}{2}}\sigma(C^{\frac{1}{2}}) + 0.237 \ C.$$

m.	$C^{\frac{1}{2}}$.	$1-g_{\text{theor.}}$	$1-\phi_{\text{exp.}}$	$1-g_{\text{exp.}}$	$\theta_{\text{exp.}}-\theta_{\text{theor.}}$
·001015	·0319	·0116	·0217	·0217	$-$·00004
·001081	·0329	·0120	·0167	·0167	$-$·00002
·001893	·0435	·0157	·0191	·0191	$-$·00002
·003115	·0558	·0200	·0195	·0195	$+$·00001
·006230	·0789	·0279	·0285	·0284	$-$·00001
·008290	·0910	·0322	·0295	·0294	$+$·00009
·016415	·1281	·0439	·0439	·0436	$+$·00002
·022811	·1510	·0511	·0516	·0512	$-$·00008
·036379	·1907	·0634	·0669	·0663	$-$·00039
·058966	·2428	·0793	·0812	·0802	$-$·00019
·063274	·2515	·0819	·0832	·0822	$-$·00007
·11351	·3369	·1080	·1097	·1079	$+$·00004

deviations between calculated and observed values are due primarily to errors in the former or to errors in the latter. In some cases, for instance the concentration range 0·01 to 0·10 for $LiClO_4$, there is a systematic deviation suggesting that our formulæ are less accurate than the

TABLE X.

Freezing-point Data of Scatchard and Prentiss
for LiO_2CH.

$$1-g = 0.374 \ C^{\frac{1}{2}}\sigma(C^{\frac{1}{2}}) - 0.140 \ C.$$

m.	$C^{\frac{1}{2}}$.	$1-g_{\text{theor.}}$	$1-\phi_{\text{exp.}}$	$1-g_{\text{exp.}}$	$\theta_{\text{exp.}} - \theta_{\text{theor.}}$
·001661	·0407	·0141	·0555	·0555	$-$·00026
·003859	·0621	·0207	·0188	·0187	$+$·00003
·006142	·0784	·0253	·0234	·0233	$+$·00004
·010577	·1029	·0317	·0315	·0313 '	$+$·00001
·014980	·1224	·0364	·0348	·0345	$+$·00011
·025351	·1593	·0442	·0460	·0456	$-$·00013
·037415	·1935	·0501	·0508	·0502	$-$·00001
·054475	·2334	·0558	·0566	·0557	$+$·00002
·078905	·2809	·0610	·0626	·0613	$-$·00009
·11198	·3347	·0649	·0683	·0664	$-$·00063

TABLE XI.

Freezing-point Data of Scatchard and Prentiss
for NaO_2CH.

$$1-g = 0.374 \ C^{\frac{1}{2}}\sigma(C^{\frac{1}{2}}) - 0.170 \ C.$$

m.	$C^{\frac{1}{2}}$.	$1-g_{\text{theor.}}$	$1-\phi_{\text{exp.}}$	$1-g_{\text{exp.}}$	$\theta_{\text{exp.}} - \theta_{\text{theor.}}$
·001668	·0409	·0140	·0094	·0093	$+$·00003
·003006	·0548	·0185	·0198	·0197	$-$·00001
·005921	·0769	·0267	·0201	·0200	$+$·00015
·009982	·0999	·0308	·0297	·0295	$+$·00005
·016956	·1303	·0378	·0343	·0340	$+$·00024
·026497	·1628	·0440	·0454	·0450	$-$·00010
·037698	·1942	·0491	·0470	·0464	$+$·00038
·059993	·2449	·0556	·0562	·0552	$+$·00009
·077829	·2790	·0588	·0600	·0587	$+$·00003
·10800	·3286	·0616	·0643	·0625	$-$·00036

measurements. On the other hand, the alternations of
sign in the deviations, in the case for instance $KClO_4$,
suggest random experimental errors of the order 2×10^{-4} °C.
Occasionally we have evidence of experimental errors
as high as 5×10^{-4} °C., as for $KClO_3$ in the molality range
0·03 to 0·04. For whether our formulæ be accurate or
not they are bound to give values lying on a smooth
curve. When there are frequent alternations of sign
in the deviations, the experimental errors must be at

TABLE XII.

Freezing-point Data of Scatchard and Prentiss
for KO_2CH.

$$1-g = 0.374\ C^{\frac{1}{2}}\sigma(C^{\frac{1}{2}}) - 0.190\ C.$$

$m.$	$C^{\frac{1}{2}}.$	$1-g_{\text{theor.}}$	$1-\phi_{\text{exp.}}$	$1-g_{\text{exp.}}$	$\theta_{\text{exp.}}-\theta_{\text{theor.}}$
·000893	·0299	·0105	·0145	·0145	$-·00001$
·002286	·0478	·0163	·0088	·0088	$+·00006$
·006046	·0778	·0249	·0247	·0246	$+·00001$
·010704	·1034	·0313	·0273	·0271	$+·00017$
·016438	·1283	·0369	·0331	·0328	$+·00024$
·021241	·1457	·0403	·0432	·0428	$-·00019$
·029945	·1730	·0451	·0425	·0420	$+·00035$
·046477	·2156	·0511	·0492	·0484	$+·00047$
·068190	·2612	·0557	·0561	·0549	$+·00020$
·093846	·3064	·0586	·0608	·0592	$-·00021$

TABLE XIII.

Freezing-point Data of Scatchard and Prentiss
for $LiO_2C.CH^3$.

$$1-g = 0.374\ C^{\frac{1}{2}}\sigma(C^{\frac{1}{2}}) - 0.210\ C.$$

$m.$	$C^{\frac{1}{2}}.$	$1-g_{\text{theor.}}$	$1-\phi_{\text{exp.}}$	$1-g_{\text{exp.}}$	$\theta_{\text{exp.}}-\theta_{\text{theor.}}$
·001842	·0429	·0147	·0267	·0267	$-·00008$
·002253	·0474	·0156	·0206	·0206	$-·00004$
·006059	·0778	·0248	·0259	·0258	$-·00002$
·010555	·1027	·0310	·0308	·0306	$+·00001$
·015196	·1233	·0356	·0319	·0316	$+·00021$
·023164	·1522	·0412	·0424	·0420	$-·00006$
·033449	·1829	·0461	·0467	·0461	·00000
·039677	·1992	·0483	·0493	·0486	$-·00004$
·055988	·2366	·0525	·0525	·0515	$+·00020$
·082635	·2875	·0559	·0565	·0551	$+·00023$
·10681	·3268	·0573	·0598	·0580	$-·00026$

least as great as the smallest of the alternating deviations.
It therefore seems likely that the accuracy of the experi-
mental data is comparable with the accuracy of our
formulæ. An experimental accuracy of the order 2×10^{-5} °C., as suggested by Scatchard, Jones, and Prentiss,
seems out of the question.

TABLE XIV.

Freezing-point Data of Scatchard and Prentiss for NaO$_2$C.CH$_3$.

$$1-g = 0.374 \ C^{\frac{1}{3}}\sigma(C^{\frac{1}{3}}) - 0.290 \ C.$$

m.	$C^{\frac{1}{3}}$.	$1-g_{\text{theor.}}$	$1-\phi_{\text{exp.}}$	$1-g_{\text{exp.}}$	$\theta_{\text{exp.}} - \theta_{\text{theor.}}$
·000682	·0261	·0092	·0091	·0091	·00000
·002214	·0470	·0158	·0252	·0252	·00000
·002878	·0537	·0178	·0167	·0167	+·00001
·005805	·0762	·0238	·0256	·0255	−·00004
·007657	·0875	·0266	·0251	·0250	+·00005
·015628	·1250	·0348	·0335	·0332	+·00009
·023479	·1532	·0395	·0417	·0413	−·00015
·037656	·1941	·0446	·0447	·0441	+·00007
·049766	·2231	·0471	·0472	·0464	+·00013
·054054	·2325	·0478	·0467	·0458	+·00040
·080874	·2844	·0495	·0509	·0495	·00000

TABLE XV.

Freezing-point Data of Scatchard and Prentiss for KO$_2$C.CH$_3$.

$$1-g = 0.374 \ C^{\frac{1}{3}}\sigma(C^{\frac{1}{3}}) - 0.290 \ C.$$

m.	$C^{\frac{1}{3}}$.	$1-g_{\text{theor.}}$	$1-\phi_{\text{exp.}}$	$1-g_{\text{exp.}}$	$\theta_{\text{exp.}} - \theta_{\text{theor.}}$
·000577	·0240	·0085	−·0024	−·0024	+·00002
·002061	·0454	·0153	·0153	·0153	·00000
·002072	·0455	·0153	·0233	·0233	−·00006
·003866	·0622	·0202	·0102	·0101	+·00014
·005497	·0741	·0233	·0213	·0212	+·00004
·008413	·0917	·0277	·0302	·0300	−·00007
·015280	·1236	·0344	·0342	·0339	+·00003
·021154	·1455	·0382	(·0455)*	(·0452)	—
·021647	·1472	·0385	·0386	·0383	+·00002
·028042	·1674	·0415	·0410	·0405	+·00010
·039445	·1986	·0448	·0415	·0409	+·00057
·041614	·2040	·0455	·0424	·0418	+·00057
·057889	·2406	·0482	·0463	·0453	+·00063
·080671	·2840	·0497	·0487	·0473	+·00071
·10750	·3279	·0488	·0510	·0493	−·00020

* Possibly a misprint for ·0355.

Computations for the nitrates were already included in our previous paper [2], but by inadvertence they were made not for the actual experimental data, but for the smoothed values given by the authors. The λ values remain unaltered. The agreement between our formulæ and the experimental values is in the case of KNO_3 rather less good for the unsmoothed than for the smoothed data. For $LiNO_3$ and $NaNO_3$, on the other hand, there is better agreement with the unsmoothed values. The method of smoothing used by Scatchard seems to us an unsatisfactory procedure. He plots his experimental values and then draws what he believes to be the best smooth curve through them. He apparently does not realize that, unless a curve is drawn to correspond to a definite analytic function, it is practically impossible to judge by inspection whether it is really smooth. For even if the curve has a continuous slope it is not truly smooth unless its curvature and all the higher differential coefficients are also continuous.

We have also applied our formulæ to the electro-motive force measurements of Brown and McInnes [6]. These authors measured the electromotive force at 25° C. of cells of the type

$$\text{Ag} \,\bigg|\, \text{AgCl} \,\bigg|\, \begin{matrix} \text{NaCl} \\ C_1 \end{matrix} \,\bigg|\, \begin{matrix} \text{NaCl} \\ C_2 \end{matrix} \,\bigg|\, \text{AgCl} \,\bigg|\, \text{Ag.}$$

By combining these data with Longsworth's data for transport numbers of the two ions in NaCl solutions of various concentrations they obtain values for the differ-ence in $\log f$ between each pair of solutions. Absolute values of $\log f$ or f can, of course, be obtained only by making some further assumption. In testing our formula on these data we arbitrarily assume agreement between theory and experiment at the molality 0·050 and then compare the values at the remaining concentrations. Brown and McInnes actually use activity coefficients on the normality scale ; we shall denote these by γ'. We use activity coefficients on the mole fraction scale (rational activity coefficients), which we denote as usual by f. The conversion from one set to the other is effected as follows. Suppose m moles or $58·45m$ grams of NaCl to be dissolved in 1000 grams of water. The molality of the solution is by definition m, while the mole fraction of either ionic species is $0·0180m/(1+0·0180 \times 2m)$. The

specific gravity of the solution (relative to pure water) is at 25° C. given by the expression $(1+0.0412m)$. The density of water at 25° C. is 0.99707, and so that of the solution is $0.99707 (1+0.0412m)$. The mass of the solution being $1000(1+0.0585m)$ grams, its volume is

$$\frac{1000(1+0.0585m)}{0.99707(1+0.0412m)} \text{ cm.}^3$$

The normality is consequently

$$\frac{0.99707m\ (1+0.0412m)}{(1+0.0585m)}.$$

Table XVI.

E.M.F. Data of Brown and McInnes for NaCl at 25° C.

$$-\log_{10}f = 0.500 \frac{C^{\frac{1}{2}}}{1+C^{\frac{1}{2}}} - 0.130\ C.$$

m.	$-\log_{10}f$ theor.	$\Delta\log_{10}f$ theor.	$\Delta\log_{10}\gamma'$ exp.	$\Delta\log_{10}f$ exp.	Difference (exp.—theor.).	f theor.
·005	·0324	·0524	·0528	·0524	·0000	·9282
·007	·0377	·0471	·0475	·0472	·0001	·9168
·010	·0442	·0406	·0410	·0407	·0001	·9032
·020	·0593	·0255	·0259	·0257	·0002	·8724
·030	·0699	·0149	·0152	·0150	·0001	·8513
·040	·0781	·0067	·0070	·0069	·0002	·8354
·050	·0848	(·0000)	(·0000)	(·0000)	(·0000)	·8226
·060	·0907	—·0059	—·0054	—·0053	·0006	·8116
·080	·0998	—·0150	—·0151	—·0149	·0001	·7947
·100	·1072	—·0224	—·0230	—·0226	—·0002	·7812

By comparing this formula for the normality with that for the mole fraction of each ionic species, we deduce that

$$\left. \begin{aligned} \frac{f}{\gamma'} &= \frac{(1+0.0412m)\ (1+0.0360m)}{(1+0.0585m)} \\ &= 1+0.0187m, \end{aligned} \right\} \quad . \quad . \quad (5)$$

or

$$\log_{10} \frac{f}{\gamma'} = 0.0081m.$$

The comparison between our formula and these data is given in Table XVI. The first column gives m the

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* There is an error in the table given by Brown and McInnes. When the molality is 0·01 the normality is 0·0099690 and the corresponding E.M.F. is —43·025. (Private communication from Dr. Brown.)

TABLE XVII.—Values of *f* for Uni-univalent

Salt.	λ.	Molality.					
		·001	·005	·01	·02	·03	·04
Standard	·000	·966	·927	·901	·867	·844	·825
HCl	+ ·240	·966	·929	·906	·877	·858	·844
LiCl	+ ·195	·966	·929	·905	·875	·855	·840
NaCl	+ ·117	·966	·928	·903	·872	·851	·835
	+ ·130	·966	·928	·903	·872	·851	·835
KCl	+ ·056	·966	·927	·902	·869	·847	·830
	+ ·072	·966	·928	·902	·870	·848	·831
TlCl	+ ·35	·966	·931	·908	·881	—	—
LiClO$_3$	+ ·243	·966	·929	·906	·877	·858	·844
NaClO$_3$	+ ·035	·965	·927	·902	·869	·845	·828
KClO$_3$............	− ·143	·965	·925	·898	·861	·835	·815
LiClO$_4$	+ ·330	·966	·930	·907	·880	·863	·851
NaClO$_4$	+ ·065	·966	·927	·902	·870	·847	·830
KClO$_4$............	− ·435	·965	·922	·892	·850	·819	—
LiNO$_3$............	+ ·226	·966	·929	·905	·876	·857	·843
NaNO$_3$	·000	·965	·927	·901	·867	·844	·825
KNO$_3$	− ·206	·965	·925	·896	·859	·832	·810
	− ·25	·965	·924	·895	·857	·830	·807
CsNO$_3$	− ·00	·965	·927	·901	(·867)	(·844)	(·825)
NaIO$_3$............	− ·35	·965	·925	·893	·853	·824	·799
KIO$_3$	− ·35	·965	·925	·893	·853	·824	·799
LiO$_2$CH	+ ·122	·966	·928	·903	·872	·851	·835
NaO$_2$CH..........	+ ·148	·966	·928	·904	·873	·852	·837
KO$_2$CH	+ ·165	·966	·929	·904	·874	·853	·838
LiO$_2$C.CH$_3$	+ ·183	·966	·929	·904	·875	·855	·840
NaO$_2$C.CH$_3$.......	+ ·252	·966	·930	·906	·877	·859	·845
KO$_2$C.CH$_3$........	+ ·252	·966	·930	·906	·877	·859	·845

Molality (cont.).						Authors.
·05	·06	·07	·08	·09	·10	
·810	·797	·786	·776	·767	·758	
·833	·824	·817	·811	·805	·801	Randall and Vanselow; Güntelberg; Harned and Ehlers.
·829	·819	·811	·804	·798	·793	Scatchard and Prentiss.
·821	·810	·801	·793	·785	·779	Scatchard and Prentiss; Harkins and Roberts.
·823	·812	·802	·795	·787	·781	Brown and McInnes.
·815	·803	·793	·784	·776	·767	Scatchard and Prentiss.
·817	·805	·795	·786	·778	·771	Adams; Hovorka and Rodebush.
—	—	—	—	—	—	Randall and Vanselow.
·834	·824	·817	·811	·806	·802	Scatchard, Prentiss, and Jones.
·814	·801	·790	·781	·772	·764	Scatchard, Prentiss, and Jones.
·797	·782	·768	·756	·744	·734	Scatchard, Prentiss, and Jones.
·842	·834	·829	·824	·821	·818	Scatchard, Prentiss, and Jones.
·816	·805	·794	·785	·777	·770	Scatchard, Prentiss, and Jones.
—	—	—	—	—	—	Scatchard, Prentiss, and Jones.
·832	·822	·815	·809	·804	·799	Scatchard, Jones, and Prentiss.
·810	·797	·786	·776	·767	·758	Scatchard, Jones, and Prentiss.
·791	·775	·760	·747	·735	·723	Scatchard, Jones, and Prentiss.
·787	·770	·755	·741	·728	·716	Adams.
(·810)	(·797)	(·786)	(·776)	(·767)	(·758)	Hovorka and Rodebush.
·778	·760	·741	·728	·713	·700	Hall and Harkins.
·778	·760	·741	·728	·713	·700	Hall and Harkins.
·822	·811	·801	·794	·786	·780	Scatchard and Prentiss.
·824	·814	·805	·798	·791	·785	Scatchard and Prentiss.
·826	·815	·807	·800	·793	·787	Scatchard and Prentiss.
·828	·818	·809	·804	·796	·791	Scatchard and Prentiss.
·834	·825	·818	·813	·808	·804	Scatchard and Prentiss.
·834	·825	·818	·813	·808	·804	Scatchard and Prentiss.

molality; the second column gives values of $-\log_{10} f$ calculated according to the formula at the head of the table; the third column gives the difference between the calculated values of $\log_{10} f$ at the actual molality and at 0·05 molality; the fourth column gives the experimental value for the difference between $\log_{10} \gamma'$ at the actual molality and at 0·05 molality; the fifth column gives the experimental value for the difference between $\log_{10} f$ at the actual molality and at 0·05 molality; the sixth column gives the difference between the experimental values in column five and the corresponding calculated values in column three; the seventh column gives the computed values of the activity coefficient f. The R.M.S. of the deviations in column six is 0·00024. This corresponds to a deviation of only 0·015 millivolts and to one of 0·0006 in f. The agreement between theory and experiment is thus excellent.

For convenience of reference we give in Table XVII. the λ values and the activity coefficients at round concentrations for all the uni-univalent electrolytes for which there are reliable data. These are computed according to formula (3) on the assumption that the λ values are the same at 25° C. as at 0° C. For TlCl and $KClO_4$ values are not given for concentrations exceeding the solubility of each of these salts. For $CsNO_3$ there are reliable data only for concentrations up to 0·01; the values at higher concentrations are enclosed in brackets because they depend on a rather drastic extrapolation. All remaining values are almost certainly accurate to 0·5 per cent. at the worst.

In conclusion we wish to emphasize that, whilst we believe our formulæ to have a high degree of accuracy up to an ionic strength of 0·1, they should be used only tentatively at higher concentrations. In some cases they rapidly become inaccurate as the concentration is increased beyond this point.

References.

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(6) Brown and McInnes, J. Am. Chem. Soc. lvii. p. 1356 (1935).

XXVIII. *On some Criticisms of the Theory of Probability.*
By HAROLD JEFFREYS, *St. John's College, Cambridge* *.

1. AS various modern writers appear to use the word
"probability" in several different senses, it needs
to be stated at the outset that I mean by it an assessment
of a degree of knowledge with respect to a proposition,
given certain data. The theory is developed in my
' Scientific Inference,' and follows on work by several
earlier writers, notably Bayes, Laplace, and Karl Pearson.
The theory has been attacked on a number of points,
mostly connected with the principles of non-sufficient
reason and inverse probability. Any detailed reply is
made difficult by the fact that critics usually content
themselves with pointing out that the theory involves
certain postulates for which mathematics gives no proof ;
some of them manage to obtain results closely resembling
those of the theory without apparently recognizing that
they are making any postulates at all, while others obtain
no results. A defender of the theory is therefore in the
difficult position of having to infer as well as he can what
the critic is thinking when the critic's statement of his
own position is incomplete on several essential points.

The theory of probability is a formal statement of
common-sense. Its excuse for existence is that it gives
rules for consistency. It does not try to justify common-
sense nor to alter its general practice ; it recognizes that
the human mind is a useful tool, but that, like other tools,
it is not necessarily perfect. The outstanding difficulty
of scientific controversy is that a man is very liable to
have one standard of validity for his own hypotheses
and an entirely different one for other people's ; but in
fact there is a considerable amount of agreement between
the scientific practice of different individuals, and if the
common features can be stated in formal terms it will
at least be possible to say whether on a particular occasion
any individual is making his decisions in accordance
with general practice or not.

The development of probability beyond the theory of
games of chance seems to have begun with Thomas Bayes.
He took the value of an expectation as his fundamental

idea, and defined probability in terms of it, whereas most earlier and later writers have proceeded the other way. His notation is not adequate for more than elementary propositions, and satisfactory ones were given only by W. E. Johnson, Keynes, Wrinch, and myself much later. I now use $P(p \mid q)$ to denote the probability of a proposition p on data q. Bayes considers the situation where we shall be given something of value a if p turns out to be true, and supposes that it is worth our while to pay something of value b for this expectation. Then $P(p \mid q)$ is defined as being b/a. It is assumed that this ratio is independent of a. It is then easy to prove the first fundamental proposition of the theory, that the probability that one of a set of mutually contradictory propositions is true is the sum of those of the propositions separately. Bayes also proves the following important proposition :

$$P(pq \mid r) = P(p \mid r)P(q \mid pr). \quad . \quad . \quad . \quad (1)$$

Suppose that we are to receive a if p and q both turn out to be true, our present data being r. Then our expectation is worth $aP(pq \mid r)$. But we may proceed by stages, testing p first and then q ; in the second stage if p has failed we have already lost our stake, but if it has succeeded p has been added to our data. Thus at the second stage we are expecting to receive a if q is true given both p and r, and the value of this expectation is $aP(q \mid pr)$. Now return to the first stage. If p is true we shall receive an expectation $aP(q \mid pr)$; if it is untrue we receive nothing. Hence our expectation before p is tested is worth $aP(p \mid r) \, P(q \mid pr)$, and this must be equal to $aP(pq \mid r)$. Equating these results we have the proposition.

Bayes's paper has been referred to in scathing terms, but I have not been able to find any evidence that any of the critics have read the first half of it, or in particular any allusion to the above argument. Practical men might perhaps be more ready to accept as an *à priori* postulate the idea that in any given circumstances there is a best way to act, or, in other words, to say that the values of expectations can be arranged in an order, rather than to say *à priori* that degrees of knowledge themselves can, which is the fundamental postulate of my ' Scientific Inference.' On the other hand, it is possible

that many that deny the latter proposition would find
no difficulty in denying the former explicitly while
continuing to order their lives as if they always knew
the best thing to do. I do not think myself that we gain
much by defining probability in terms of expectation
rather than conversely, but whichever course we adopt
the above argument needs consideration. It appears
that the " value " for this purpose does not mean neces-
sarily a monetary stake ; other values have to be com-
pared with money in actual life, and when we spend
money for one purpose rather than another we are thinking
of the expectations of benefit in the two circumstances.
Further, to a man with an income of £500 a year the loss
of £500 would be a serious matter, while he might gain
£500 without greatly altering his arrangements ; it
would be folly for him to stake £500 on an even chance.
Yet the Anglo-Iranian Oil Co. or Imperial Chemical
Industries could do so safely. It appears that in monetary
terms the proportionality of the value of the expectation
to the stake can hold only within a limited range of the
stake in comparison with the reserves. For a complete
theory of expectation it is therefore only within limits
that the consideration of monetary stakes combined
with proportionality is enough. A much more general
theory has, however, been given by F. P. Ramsey *,
starting simply with the postulate that expectations
of benefit can be arranged in an order. He succeeds
in proving the fundamental proposition given above ;
but he still has to assume uniqueness (foot of p. 179), and
therefore does not avoid my fundamental postulate.

Wrinch and I, without using expectation, proved the
proposition (1) for the case where p and q are combinations
of equally probable and mutually exclusive alternatives,
but took it as a postulate for other cases †. It can be
seen easily, however, that it is reasonable by considering
some special cases. If p cannot be true given r, then
p and q cannot both be true ; hence $P(p \mid r)$ and $P(pq \mid r)$
both vanish and both sides are zero. If q is certain
given p and r, p and q will both be true if p is ; hence
$P(pq \mid r) = P(p \mid r)$, and $P(q \mid pr) = 1$, so that the equation
holds. If q is impossible given p and r, p and q cannot
both be true if r is ; hence $P(pq \mid r) = 0$ when $P(q \mid pr) = 0$,

* 'Foundations of Mathematics,' Chapter VII. (1931).
† Phil. Mag. xxxviii. pp. 715–734 (1919).

and the equation is true. If p is certain given r, then pq is true whenever q is ; hence $\mathrm{P}(pq \mid r) = \mathrm{P}(q \mid r)$. But in these conditions if r is among the data p is implied. Hence $\mathrm{P}(q \mid r) = \mathrm{P}(q \mid pr)$, while $\mathrm{P}(p \mid r) = 1$, and again the proposition is verified. It therefore holds in all the four extreme cases, as a perfectly general proposition independent of our postulate about the nature of p and q.

It should be noticed that if we try the alternative form

$$\mathrm{P}(pqr) = \mathrm{P}(p \mid r)\mathrm{P}(q \mid r) \quad . \quad . \quad . \quad (2)$$

we get the right result in the first and fourth of the above cases ; but in the second we get agreement only if $\mathrm{P}(q \mid r) = 1$, and in the third if $\mathrm{P}(p \mid r)$ or $\mathrm{P}(q \mid r)$ is 0. This form is therefore less general. It is correct only when $\mathrm{P}(q \mid pr) = \mathrm{P}(q \mid r)$ or when p is impossible. The former alternative says that the truth of p gives us no information about that of q, a special case.

From proposition (1) Bayes proves the principle of inverse probability, namely, that if $p_1 \ldots p_n$ are a series of alternative hypotheses whose probabilities are to be assessed on data q and h, $\mathrm{P}(p_r \mid qh)/\mathrm{P}(p_r \mid h)\mathrm{P}(q \mid p_r h)$ is independent of r. The method is substantially the same as in several recent works, and need not be repeated. Laplace seems to have adopted this principle directly, and it is perhaps for this reason that it is often referred to as an unjustified assumption. At any rate I know of no reference to Bayes's proof. Of the two text-books of algebra in my possession Hall and Knight prove it by stating Bernoulli's theorem (see next section) without proof and applying it to a large number of trials ; C. Smith does the same without mentioning Bernoulli, his theorem being given only as a very loose discussion, involving three different definitions, in the first paragraph of the chapter. Indeed, anybody that got his first ideas about probability from this paragraph can easily be forgiven for failing to understand it. In any case the method is needlessly cumbrous, even in Hall and Knight. Bernoulli's theorem depends on the special case where (2) holds, and cannot be proved without reference to the foregoing theory, whereas the principle of inverse probability can be proved directly.

2. The principle of non-sufficient reason is simply the formal way, in accordance with our definition, of saying

" I do not know." If we have no information to enable us to express any choice between different alternatives, their probabilities are equal. If there are $a+b$ alternatives, all equally likely, as far as our previous knowledge goes, the probability of any particular one is $1/(a+b)$, and the probability that one of the a will be true is $a/(a+b)$. This statement, which is common to all theories, is often assumed to be equivalent to the statement that if we make a very large number of trials the fraction of them that will give an a will tend in the limit to $a/(a+b)$. As an example consider a deal at bridge. The ace of spades is equally likely to come to any one of the four players; hence the probability that a particular player will get it is $1/4$ by the principle. The second statement is that if this player takes part in n deals he will receive the ace of spades $\frac{1}{4}n+k_n$ times, where k_n/n tends to 0 as n tends to infinity. The curious thing is that this result is taken as an obvious statement of fact by people that professedly reject the principle of non-sufficient reason. It is not an experimental fact, because any player has taken part in only a finite number of deals. It cannot be proved mathematically, because it would be possible for the same player to get the ace of spades every time ; there is nothing in the conditions to prevent it. The only reason for believing it rests on a theorem due to James Bernoulli. If the probability of an event at every trial is p, and is unaffected by the results of previous trials, and α and β are two given positive numbers, however small, the probability that the event will occur between $n(p-\alpha)$ and $n(p+\beta)$ times in n trials can be made as near unity as we like by taking n large enough. The postulate and the conclusion are both in terms of probability, which is therefore a more primitive idea than the existence of the limit. Yet many writers, following Venn, take it for granted that in the limit the event will occur in just a fraction p of the trials, p being the probability at one trial given by the principle of non-sufficient reason, and at the same time deny the very principle that provides their only justification. Some, including Venn himself, take the limiting ratio as the definition of probability ; this avoids the reference to a degree of knowledge, which many call " metaphysical " or " psychological," but at the cost of making it impossible to attach a definite value to any single probability, because without using Bernoulli's

theorem there is no means whatever of determining the
value of the limit in terms of anything we know.   On
Venn's definition we cannot say that the probability of
getting the ace of spades is $\frac{1}{4}$ until we have made an
infinite number of deals.   An alternative way of avoiding
the mention of degree of knowledge is to define the proba-
bility directly in terms of numbers of combinations.
Thus of the 52 ! possible ways of dealing a pack 13×51 !
will give the ace of spades to an assigned player, and the
ratio is $\frac{1}{4}$.   Unfortunately this method rejects the very
thing that we want to know.   Working out such ratios
may be a harmless mathematical exercise, but if a
player wants to know how often he will get this card in
100 deals what can they tell him ?   Simply that in
the $(52 !)^{100}$ series of deals that might occur there are

$$\frac{100 !}{m!(100-m) !}\left(\frac{1}{4}\right)^m\left(\frac{3}{4}\right)^{100-m} (52 !)^{100} \text{ that would give it to}$$

him m times ; there the argument stops.   He can if
he likes say that all deals are equally likely ; then
he will apply the principle of non-sufficient reason, infer
that the probability of any particular value of m is

$$\frac{100 !}{m !(100-m) !}\left(\frac{1}{4}\right)^m\left(\frac{3}{4}\right)^{100-m}, \text{ and hence that the probability}$$

of getting the ace of spades between 20 and 30 times is high.
The point is that the method is of no use for prediction
until the principle of non-sufficient reason is brought
in ; anybody offering such a definition cannot consistently
give advice, and if he presents his results in such a form
while declaring that the principle of non-sufficient reason
is meaningless or untrue he is saying that application of
them to any concrete problem is invalid.   It is a curious
fact that those who adopt this definition are not less
inclined to give advice than others, but as they do not
state what they substitute for the principle of non-
sufficient reason one may suspect that they are using it
as a common-sense notion, which it is, without noticing
that it is not included among their stated postulates.

3. The principle of non-sufficient reason was also
applied by Bayes and Laplace to the prior probability
in sampling.   Considering a bag with n balls in it, they
said that if the number of white balls in it is r, and we
have no previous information about the value of r, the

probabilities of all values of *r* are equal. This is, as before, merely an expression of the fact that *r* is unknown. Many, however, including three speakers at the recent discussion at the London Mathematical Society, have declared that to say that we know nothing about *r* is to say that we cannot assess its probability at all. These statements, however, are quite different. Probability being a statement of knowledge, the first is " I know nothing about *r*" ; the second is " I do not know whether I know anything about *r* or not." If the second really represents anybody's state of mind it seems useless to try to help him.

This difficulty seems to me entirely spurious. Nevertheless there is a real difficulty about the Bayes-Laplace assessment. If the probability of there being, in a class of *n*, just *r* members with a certain property is always $1/(n+1)$, before a sample is taken, we could apply Bernoulli's theorem and say that out of a large number of such classes a fraction nearly $1/(n+1)$ will be almost certain to have the property that interests us. This is plainly something that cannot be asserted without observational evidence. The mistake lies not in the notion of prior probability, but in the assumption underlying Bernoulli's theorem, that equation (1) can be replaced by (2). In deals at cards this assumption is correct, one deal, with proper shuffling, giving no information about the next, and the theorem holds ; but it must be said again that Bernoulli's theorem refers to very special circumstances. It is altogether exceptional for the probability of a proposition to be so fixed that no further information will alter it. If we get absurd results by using the theorem it shows that these circumstances do not hold in the problem being considered. But to reject the result implies that the observed composition of one class affects the distribution of the prior probability in another. If we find that the observed values of *r* in different classes are concentrated towards the ends of the range, for instance, we must consider this a real property of the world and allow for it in assessing the prior probabilities in new classes.

Bayes and Laplace, combining their statement of ignorance of *r* with the observed composition of a sample, by means of the principle of inverse probability, compared the probabilities of the possible compositions after the sample is taken. On the whole the results agree with

ordinary belief, and it was only a long time afterwards that Pearson (in the ' Grammar of Science ') and Broad noticed that on their assessment the proposition that all or none of the members had the property under discussion would never acquire a reasonably high probability until nearly the whole of the members had been examined. Bayes and Laplace took the prior probabilities in the extreme cases to be the same as for any other number, with the result that according to their estimate it will never be possible to establish a general law on any amount of evidence that is ever available. Everybody in fact believes a large number of general laws, and as the function of the theory is to give a consistent statement of common-sense, and not to alter it in a fundamental respect, it appears that the estimate of Bayes and Laplace needs modification for the extreme cases. This was attempted by Wrinch and myself in 1921 for quantitative laws, in which the difficulty enters in a specially acute form ; but we pointed out that agreement with general belief is obtained if we take the prior probability of a simple law to be finite, whereas on the natural extension of the previous theory it is infinitesimal. Similarly for the case of sampling J. B. S. Haldane and I have pointed out that general laws can be established with reasonable probabilities if their prior probabilities are moderate and independent of the whole number of members of the class sampled. These rules have been called " simplicity postulates " ; they do not say that any particular simple law must be true, or even that some simple law must be true, but they do say that when we consider a simple law seriously an assessment of the prior probability that will make it impossible ever to establish it even if it happens to be true is not a correct representation of our state of knowledge.

It appears that at the present stage of scientific knowledge the prior probability of a simple quantitative law or a general one is not assessed *a priori* (that is, independently of experience), though it must have been in the earliest stages and in the early life of any individual. It is inferred from the frequency of verification of such rules in the past. The principle that it is finite stands, and with it most of the arguments in my ' Scientific Inference.' But the suggestion on p. 46 of my book that it is worth while to determine the number of possible

quantitative laws of complexity, as there defined, less than a certain value, and to state their prior probabilities accordingly, ceases to have much interest. Incidentally this disposes of the statement that the prior probability is unknown; it is a perfectly determinate quantity that could be found by taking enough trouble. However, the trouble would be considerable, and the type of consideration mentioned on p. 23 arises, that if a man trying to catch a train stops to calculate the probability of catching it, allowing for all the relevant data, he will certainly miss it. It is more profitable in a given time to take some extra relevant observations than to evaluate accurately a prior probability that in any case will not express any strong preference between the alternatives that we do in fact consider seriously. For practical purposes what we need is not an accurate determination of the prior probability, but an approximate working rule.

Actual sampling ratios are reasonably uniformly distributed from 0 to 1, apart from the extremes, and therefore in a new class sampled, if there is no special information, we can take the prior probability as uniformly distributed. For general and quantitative laws I suggest simply that all alternatives seriously suggested at any one time should be given the same prior probability. It is this that I have used in tests of significance. In the case of quantitative laws an added degree of complexity usually means the introduction of a new term with an adjustable coefficient; we take it to be initially as likely as not that such a term is present, and on the hypothesis that it is present take the prior probability of the coefficient as uniformly distributed within the range permitted by the residuals outstanding. The results show that the probability that such a term is needed is increased or decreased according as the coefficient is more or less than a certain multiple of its standard error; the multiple needed, however, increases with the number of observations. Any subject in the natural course of its development will then provide its own means of redetermining the prior probabilities of general or simple laws. I have discussed elsewhere * the question of the possible revision of a law when data become more numerous or more accurate.

* Proc. Camb. Phil. Soc. xxxii. 1936 (in the press).

·In this discussion no reference is made to the possibility that the list of alternatives thought of may be incomplete, which raises the logical problem of the " excluded middle." One reason is practical : we cannot lay down rules to cover possibilities that nobody has thought of, nor can we say how to test them.   The excluded middle term leads to no one inference rather than another until it is definitely stated, and when compared with laws that lead to numerous or accurately verified inferences its posterior probability is always negligible *.   When the verifications are few the laws stated may have only moderate probabilities, and it is only then that the excluded middle is worth considering. The situation is, of course, altered completely if at any later date an unconsidered alternative is put in a form that leads to verifiable inferences.   Then we can consider whether it is, from an observational point of view, a new hypothesis or a subdivision of one considered already. In either case we can reassess the prior probabilities taking it into account, and determine the posterior probabilities afresh.   The answer to anybody who says that we have not discussed all possible theories is " produce a better one."

This attitude differs from that given on p. 51 of my book, where I suggested that Asaph Hall's modification of the index in the law of gravitation to explain the motion of the perihelion of Mercury should have been discarded at sight ; though I still maintain that the addition of an inverse cube term should have been tried, and this would have given results consistent with the motion of the moon.

The question now arises whether the application of Bernoulli's theorem leads to unacceptable results for measured quantities.   Thus in measurement of a length the prior probabilitiy of the true value is taken uniformly distributed over a wide range, while for some essentially one-signed quantities, such as standard errors, that of the logarithm is taken uniformly distributed, also over a wide range.   These are statements of ignorance ; if measures give no information relevant to future experiments we can apply the theorem, and say that the true values will in the long run be uniformly distributed in frequency and that standard errors also will be distributed so that the number per unit increase in the logarithm

will be uniform. It appears that this is sometimes true and sometimes not. Thus an observer may be suspected of a tendency to a preference for reading one final figure rather than another when he is reading to tenths of the scale interval ; and he may test this by reading a large number of lengths, and seeing whether all final digits occur nearly equally often. This indicates that there is considerable confidence in the result, at least over several scale intervals. But these laws involve a proportionality factor, and there are in general restrictions above and below on the values possible, which differ from one type of experiment to another, and the probability of a value within any particular range is not always the same. Hence the theorem is not applicable in such cases. On the other hand, for measurements of the same kind a standard error found in one series does provide information relevant to that to be expected in a new series.

4. In a paper by Sir Arthur Eddington * we find on p. 272 the statement that " the accepted risk will vary according to the purpose for which the determination is to be used and the rashness of the user. A risk of 1/6, corresponding to an allowance of double the probable error, is perhaps the most usual allowance for ordinary purposes ; but a navigator determining his position at sea would not be satisfied to run his ship on the rocks once in six times." Here Eddington is comparing the desirability of various courses of action, allowing for the amounts at stake ; in other words, he is thinking in terms of the values of expectations. But once granting that expectations are comparable, we can define probability by the methods of Bayes and Ramsey.

Again, on p. 274, where Eddington is discussing least square approximations, he says " If the actual error of μ_r is ϵ_r, . . .

$$\text{error of } x(=\Sigma_r\lambda_r\mu_r)=\Sigma\lambda_r\epsilon_r \quad . \quad . \quad . \quad . \quad (3)$$

and by a well-known theorem (not assuming the Gaussian law)

$$\text{mean square error of } x=\sqrt{(\Sigma\lambda_r^2)}\epsilon, \quad . \quad . \quad (4)$$

where ϵ is the mean square error of μ_r (the same for all the μ_r's as already stated)." Now when we inspect the proof of this theorem † we find that it depends on the

* Proc. Phys. Soc. xlv. pp. 271–282 (1933).
† *Cf.* Brunt, ' Combination of Observations ' p. 37 (1931).

statement that if we have a very large number of observations the sum of the products of errors of the form $\epsilon_r \epsilon_s (r \neq s)$ will in the long run be small compared with those of the form $\epsilon_r{}^2$, the stated reason being that positive and negative errors like ϵ_r and ϵ_s are equally likely to be associated. In other words, it is supposed that the sign of ϵ_r gives no information about that of ϵ_s, however many instances have occurred already, and Bernoulli's theorem is applied to say that in the long run positive and negative products will occur about equally often and cancel. But Bernoulli's theorem rests on the numerical assessment of probabilities corresponding to degrees of knowledge, which is therefore implicit in Eddington's discussion.

Eddington then proceeds to attack the postulate of the theory of measurement that the prior probability of the true value is uniformly distributed. He says :—" The argument that, because the consequences of hypothesis A turn out to be more probable than those of hypothesis B, therefore hypothesis A is more probable than hypothesis B, cannot be accepted without qualification. Having tossed a penny 5 times in succession we observe that it has come down heads every time ; this occurrence is much more probable on the hypothesis that it is a double-headed penny than on the hypothesis that it is an ordinary penny, but it does not follow that it is more probably a double-headed penny than an ordinary penny. It is true that in rejecting the argument we are guided not only by the ostensible data of the problem but by private knowledge that double-headed pennies are rare ; but the real point is that questions of inverse probability are of such a nature that they compel us to introduce private knowledge or prejudice . . . since otherwise there is no answer to them. The objection to inverse probability is not so much that it is invalid as that it is silly."

In this astonishing argument Eddington obtains the correct answer by using inverse probability, and immediately says that it is silly. The fact is that the experiment as stated would be useless for the purpose of deciding whether the penny was an ordinary one, because the additional information given by it is overwhelmed by the previous knowledge. Using my own knowledge for the purpose, I suppose I have looked at both sides of some tens of thousands of pennies in my life, and have

always found the sides different ; the probability that the next will be double-headed is therefore less than 1/10000 *. On the hypothesis that this particular penny is double-headed the result of the experiment has probability 1 ; on the hypothesis that it is ordinary the corresponding probability is 1/32. Combining these with the prior probability we see that the posterior probability that it is double-headed is under 1/300. Before such an experiment could show an appreciable probability that the coin was double-headed it would have to be thrown about 30 times instead of 5. On the other hand, a Central African unfamiliar with British coins would infer perfectly legitimately that the coin was probably the same on both sides ; we should not agree with his inference, not because it is based on an incorrect procedure, but because we have more relevant data. On p. 281 Eddington returns to the subject, and suggests that " if we habitually infer when the first 5 throws turn up heads that the penny is double-headed we shall be wrong only once in 32 times, and perhaps not then if double-headed pennies exist. Thus in the long run we shall not be wrong more than once in 32 times." Bernoulli's theorem is again being used, also the principle of non-sufficient reason, saying that in any trial either side is equally likely to turn up. If Eddington had acted on such a principle he would have rejected Einstein's law of gravitation. The motion of the node of Venus, which was rendered inexplicable by this law, represents in relation to its standard error a 1/2500 chance that has come off ; but on my theory it supports the law against any special hypothesis introduced only to explain it. The fact is that to try to make inferences without allowing for obviously relevant data is to ask for trouble. In the above case when the first five throws give heads he would be wrong every time.

Apparently, according to Eddington, since previous knowledge must not be used, every set of observations must be discussed separately, and none gives information relevant to the treatment of any other. Yet he mentions later that some ways of finding the charge on the electron give e, others e^2. But on his own argument there is not the slightest reason to believe that what is called e is the same thing in the two types of experiment ; any belief

* This is on Laplace's assessment ; if we allow an appreciable prior probability that all pennies are alike the value will be smaller.

that may exist rests on previous theoretical arguments or on the experimental fact that what is found in one is nearly the square of what is found in the other.

He has recently repeated this argument with little alteration in ' New Pathways in Science,' but " private knowledge or prejudice " is repeatedly replaced by " secret knowledge " ; and here, I suspect, we come to the core of the matter. Why should previous knowledge be secret ? We might tell the above Central African of our experiences with regard to pennies, and other Englishmen have had previous experiences similar to Eddington's. The Central African's knowledge is then increased by the report of somebody else's experience, and he can reassess his probability accordingly. This is subject to his belief in our veracity ; but this in turn rests on the fact that people do habitually use the same words in similar circumstances. If there was no such agreement nobody would ever learn to speak intelligibly at all, much less to understand anybody else's language. The probability on any ordinary occasion that a person is reporting his experience correctly is in fact very nearly unity. So long as relevant knowledge remains secret different people will necessarily assess different probabilities ; but that is no argument against the theory of probability, but against the practice of people arguing without telling one another what their data are. Eddington's own theoretical work in other fields depends mostly on accepting other men's observations.

On p. 279 of the above paper Eddington says : " This difficulty [about the prior probability] in the usual theory of least squares arises because it mixes up two distinct subjects, viz., the combination of observations and the philosophy of inference from observation. The presentation here adopted avoids the difficulty entirely because it sticks strictly to the combination of observations." This is untrue. Bernoulli's theorem, which rests on the definition of probability as degree of knowledge, has been used repeatedly ; two cases have been mentioned above, but wherever the phrase " in the long run " occurs in the paper the theorem is being used. So has the principle of non-sufficient reason. Expectation has been introduced at an early stage and used as one reason for using the mean square error as a standard of accuracy. The other reason given for using the mean square error is that the

linear spread for a given risk of error is proportional
to it ; thus the possibility of making inferences has
determined the whole structure of the paper. In fact
everything needed to construct a theory of probability
and apply it to the combination of observations has
been assumed, and the only omission has been to apply
it systematically.

This paper of Eddington's has been chosen for discussion
here because in comparison with other attempts to avoid
the theory of probability it shows more clearly what the
author is thinking when there is a gap in the argument,
and reveals how easily the hypotheses of the theory can
be used without being noticed, and how, after being used,
they may be forgotten.

5. As a simple specimen of a significance test I shall
take the experiment of a wheel rolling down an inclined

s.	t.	$s^{\frac{1}{2}}$.	t_1.	$t-t_1$.	t_2.
5	67, 68, 70, 70, 69, 67	3·87	68·2	$-1·2, -0·2, +1·8, +1·8, +0·8, -1·2$	68·3
2	60, 61, 59, 61, 61, 61	3·46	60·9	$-0·9, +0·1, -1·9, +0·1, +0·1, +0·1$	61·0
0	56, 56, 55, 56, 57	3·16	55·6	$+0·4, +0·4, -0·6, +0·4, +1·4$	55·7
8	50, 50, 51, 50, 50	2·83	49·8	$+0·2, +0·2, +1·2, +0·2, +0·2$	49·8
6	43, 43, 44, 43, 42	2·45	43·1	$-0·1, -0·1, +0·9, -0·1, -1·1$	43·1
4	35, 35, 34, 36, 35	2·00	35·2	$-0·2, -0·2, -1·2, +0·8, -0·2$	35·2

plane mentioned on pp. 37–41 of my book. The data
as given there are simplified ; here I use the actual ones
that I once obtained as a student. The uncertainty
of the time to a given distance can be considered uniform,
while that of the distance at a given time is not, on account
of the variation of velocity. The units are 10 cm. for
s, 0·2 sec. for t.

With uniform acceleration from rest t should be pro-
portional to $s^{\frac{1}{2}}$; hence we try $t=as^{\frac{1}{2}}$ and solve for a by
least squares. The solution is $a=17·61$; t_1 gives the
calculated times. Only 7 residuals out of 32 exceed the
step of the scale, which is therefore apparently a main
source of error. But as this is only an illustration we
may as well proceed as if the normal law of errors held.
The mean square residual is 0·85, and the standard error
of a is $0·85/(\Sigma s)^{\frac{1}{2}}=\pm 0·05$.

Our first doubt may be about whether t is affected by an additive constant, such as might be due to a difference between the times needed to start and stop the watch. If there is such an effect we must write $t = as^{\frac{1}{2}} + b$. The normal equations for a and b are now

$$\left. \begin{array}{l} nb + a\Sigma s^{\frac{1}{2}} = \Sigma t \\ b\Sigma s^{\frac{1}{2}} + a\Sigma s = \Sigma t s^{\frac{1}{2}} \end{array} \right\} \quad \left. \begin{array}{l} 32\,b + 96 \cdot 22\,a = 1695 \\ 96 \cdot 22\,b + \quad 302\,a = 5320 \cdot 9 \end{array} \right\},$$

whence $a = 17 \cdot 68$, $b = -0 \cdot 19$. The resulting calculated values are t_2. The mean square residual is reduced to $0 \cdot 82$. The standard error of b can be got by the following device. Put 1 on the right of the first normal equation, 0 on the right of the second. Then the solution is $b = 0 \cdot 72$, and the standard error of b is $0 \cdot 72^{\frac{1}{2}} \times 0 \cdot 82 = 0 \cdot 70$. Thus the estimated b ($= -0 \cdot 19$) is less than its standard error and is not significant ; that is, the observations by themselves do not support the hypothesis that b is different from 0. When one unknown is determined at a time by least squares the criterion * that the last determined shall be supported by the observa-ⁿons is that

$$\frac{b^2}{\sigma_b{}^2} > \log_e \frac{2n}{\pi},$$

where n is the number of observations. Here $n = 32$, and for b to be significant we should have to have $b/\sigma_b > 1 \cdot 74$. In the present case b/σ_b is unusually small. If the probability that $b = 0$ is $\frac{1}{2}$ before the observations, it is $0 \cdot 8$ after them.

A further approximation has been sought in the form $t = as^{\frac{1}{2}} + cs$. It gives $c = +0 \cdot 07 \pm 0 \cdot 87$, so that again the observations are against its reality.

The following table gives the critical ratios that an unknown found by least squares from n observations shall be supported by the observations.

$n.$	$b/\sigma_b.$	$n.$	$b/\sigma_b.$	$n.$	$b/\sigma_b.$
5	1·07	200	2·20	10,000	2·96
10	1·36	500	2·40	20,000	3·07
20	1·59	1000	2·54	50,000	3·22
50	1·86	2000	2·67	100,000	3·33
100	2·04	5000	2·84		

* Proc. Camb. Phil. Soc. 1936 (in the press).

It should be said that the establishment of a simple law by this criterion is in a sense temporary and not final. The method considers as equivalent alternatives that the residuals are entirely due to random errors and that they are partly due to random errors and partly to a systematic effect with an unknown coefficient. The above criterion determines when the observations support the first or the second hypothesis. Simplicity is here a matter of the number of parameters that we are trying to determine from the observations. It needs to be noted that if the number of observations is small the support for a simple law cannot be strong, though they may give strong evidence against it. Thus if the prior probability is $\frac{1}{2}$, and $n=5$, the posterior probability cannot exceed 0.65; but if $n=10,000$ it may reach 0.988. If there are only two observations of unknown accuracy there is no way of deciding how much of the difference between them is due to random and how much to systematic variation, and no criterion can be obtained. This is one reason for using a large number of observations. On the other hand the method does little or nothing to decide between slightly different laws containing the same number of adjustable constants. If an accurate measurement disclosed that in the above experiment the runners were not quite plane, we should still be able to say that only one parameter can be found from the observations, though before assessing its value we should be entitled to allow for the known curvature of the path.

The usual practice has been to regard a departure from a simple law as genuine if it amounts to some constant multiple of the standard error, usually 2 or 3 times. The ratio given above is not constant, but depends on the number of observations. If a ratio of 2 or 3 is really needed when the number is small, it expresses a prior belief in the simple law to the extent of saying that the odds in its favour are 6 to 1 or 90 to 1, or else a criterion of convenience that we must not complicate future computations except for specially strong reasons. In either case corresponding, but smaller, increases would be needed throughout the table. When the number of observations is large the critical ratio exceeds the arbitrary standard, which will thus for 100,000 observations lead to coefficients between 2 and 3·33 times their standard errors being accepted as genuine, when in fact the observa-

tions render them less probable than before. Thus there will be mistakes in all cases where there is no real departure and yet the computed departure is between 2 and 3·33 times its standard error. Fortunately the latter event does not occur very often ; nevertheless it has arisen.

Apart from this theory there appears to be little reason for ever rejecting a term found by least square approximation. If any value of the coefficient of the new term is equally admissible the most probable is that actually found by least squares, which also gives Fisher's maximum likelihood, and the rejection of it, however small it may be, is arbitrary, and will be expected in most cases to reduce the accuracy of further inferences. On the present theory, on the other hand, a coefficient less than the critical value is evidence that the term is either absent or has a coefficient substantially under its standard error, and we shall expect to get more accurate inferences by rejecting it. On the former views, when a term is comparable with its standard error there is no apparent reason for expecting it to decrease rather than to increase when the observations are made more numerous or more accurate ; on mine we shall expect it usually to decrease. The fact that the latter result has usually occurred in practice may be the immediate basis of current custom, which therefore rests on an inductive inference of the type covered by the theory of probability. The theory provides an explanation of current practice, though it gives a more detailed criterion of significance. It provides in particular a reason against the practice of determining periodicities by harmonic analysis and publishing them without regard to their uncertainties.

6. In statistical practice " significance " is used in the above sense and also in another. The latter may be illustrated by considering an examination consisting of 100 questions of uniform difficulty selected from a much larger number that might have been asked according to the syllabus. A candidate whose ability covers half the syllabus is most likely to answer 50 questions correctly, but the random selection of questions will cause the probability of the number that he answers to be distributed about 50 with standard error 5. Then if candidate A actually answers 50 questions, and B 49, it is more

probable that not that A knows more than B, since we
already know that candidates are not all of equal ability.
A difference of one mark is significant in the above sense.
Actually most statisticians would say that it is not
significant, so that the word is being used in a different
sense. They would in most cases put the limit at a
difference of about 10 questions, which means that on the
data they do not require merely to say that A is probably
better than B, but that it is almost certain that he is.
This criterion, then, is not purely a matter of probability.
The division of candidates into classes is a compromise ;
it aims both at stating differences between individuals
and at avoiding mistakes completely, and these ends are
not consistent. The largest number of real differences
would be given correctly if the whole list was published
in order of merit ; all mistakes would be avoided only by
passing everybody without discrimination. The actual
method represents therefore a balancing of expectations
of value ; the desirability of stating differences between
individuals is weighed in psychological terms against
that of avoiding injustice to any one individual. If the
upper limit of the second class is at 65 per cent., the
method fails in the first respect, since the actual merits
of two candidates may be 64 and 66 per cent., and yet
they may both get 66 per cent. of marks and appear in
the same class ; and in the second because two candidates
whose merits are both 66 per cent. may actually get
70 and 63 per cent. of marks and appear in different
classes. No method could avoid both these objections.

Now in my sense the assertion that a coefficient exceeds
the critical value is an assertion that on the data the
hypothesis that it is real is more probable than not,
and therefore is of the same form as the statement that
a candidate with 50 marks probably knows more than
one with 49. If the undesirability of asserting differences
without strong evidence is a factor in this problem also,
the value needed to entitle us to assert a difference must
be increased ; but this, as for the examination problem,
is a matter of what we want and not of pure theory of
knowledge. Possibly this undesirability could be estimated
quantitatively by comparison with what people consider
a satisfactory level of significance in simple cases where
differences are known to exist, as for examinations, and
could then be allowed for. Nevertheless it would be

impossible to replace the above table of critical values by any other table of single entry. The complete theory gives the ratio

$$\frac{\mathrm{P}(p \,|\, qh)}{\mathrm{P}(\sim p \,|\, qh)} \bigg/ \frac{\mathrm{P}(p \,|\, h)}{\mathrm{P}(\sim p \,|\, h)},$$

where p is the simpler hypothesis and $\sim p$ the more complicated one to be tested, h the previous knowledge, and q the immediate observational data. If p and $\sim p$ are equally probable initially, and we consider it undesirable to assert $\sim p$ until $\mathrm{P}(p \,|\, qh)/\mathrm{P}(\sim p \,|\, qh)$ has dropped to 1/6, say, we could construct a table of the critical ratio for this limit; but if one experiment made $\mathrm{P}(p \,|\, qh)/\mathrm{P}(\sim p \,|\, qh)$ equal to 1/3 and another $\mathrm{P}(p \,|\, rh)/\mathrm{P}(\sim p \,|\, rh)$ equal to 1/2, the information provided by the two together would usually make $\mathrm{P}(p \,|\, qrh)/\mathrm{P}(\sim p \,|\, qrh)$ equal to 1/6, though neither separately would satisfy this criterion. To use a single table for a ratio 1/6 would therefore fail to represent either our knowledge or our wishes.

The above remarks suggest a possible solution of the examination problem. The usual division is into three classes and failure, but some examinations attempt closer divisions. Now if the second class ranges from 45 to 65 per cent., a candidate whose real ability is 55 per cent. is practically certain to be correctly placed; but one whose ability is 65 per cent. is hardly more likely to be placed correctly than not. The chance of injustice therefore operates very unequally on different candidates, and this could be avoided only by publishing an order of merit. But if the undesirability of asserting the wrong differences in comparison with that of failing to notice real differences can be put into a quantitative form there will be a best number of classes to make. Thus if there is value 1 for asserting a difference with the correct sign, 0 for not asserting it, and -5 for asserting it wrongly, we shall realize our desires best by choosing the number of classes so that the total value of our expectation is a maximum. It will be positive if over 5/6 of the differences asserted are correct.

7. A probability unaffected by the results of previous trials has been called a " chance " by N. R. Campbell and M. S. Bartlett. It is only to such probabilities that

Bernoulli's theorem is correctly applicable. Campbell has maintained that the existence of chances can be shown by experiment. This appears to be possible when significance tests are applied. The existence of chance must be distinguished from absence of bias. Thus Campbell has recently published the results of 500 throws of a coin *. To test the absence of bias we should have to examine whether the observed number of heads differs from 250 by enough to increase the probability that the chance of a head differs from $\frac{1}{2}$; but even if it does so there may still be a chance. To say that chance exists is to say that the probability of a head at any trial is independent of the results of previous trials. I have not obtained a general test for this, but it is possible to obtain a rule for testing whether it is independent of the trial immediately before, and this may be enough for the purpose. Such a rule has been applied to the distribution of earthquakes in time, testing whether the observed frequency with which an earthquake in one region is followed by one in another region is such as can be attributed to chance.

According to the usual theory of errors the accuracy of a determination increases indefinitely with the number of observations. Campbell contests this, saying that beyond a certain number the accuracy decreases, and that the best number to take is best determined by the physicist's judgment. On the whole I should agree with him, though I should amplify the last remark a little. The normal law of errors depends on two facts †. It agrees fairly well with the observed frequency of errors in many cases, though it usually breaks down at about twice the standard error of one observation ; and it can be inferred, subject to the same restriction, if the error is the sum of a moderate number of comparable and independent parts. But neither of these arguments gives any reason for supposing that the mean of the distribution of chance is the true value (in my language, not Campbell's) or that the mean of a large number of observations will in the limit approach the true value indefinitely closely. On the experimental side what is observed may be the sum of the true value and some constant that depends on the method of experiment ; on the theoretical side the laws of the component errors need not be symmetrical

* Proc. Phys. Soc. xlvii. pp. 800–809 (1935).
† Proc. Camb. Phil. Soc. xxxi. pp. 207–210 (1935).

and may give means different from zero. These are absorbed into the true value by a convention in the course of the proof, and thenceforward usually forgotten *, but they provide a theoretical reason why the mean may be displaced from the true value in the way just suggested. This is the "systematic error." It is well recognized as affecting the comparison of different sets of observations ; but it is evidently possible that it may vary within a single set, if for instance the observer becomes tired or the apparatus wears. Both of these are matters for the observer's judgment, and he is entitled to give special weight to the observations made in the best conditions. But his judgment may be supplemented from the observations themselves. Instead of treating them as a single series all of equal precision, he can divide them into sets arranged in order of time and find a mean and a standard error from each set. Then the differences between the means can be tested for significance. So long as they are not significant the sets can then be combined, using weights found from the standard deviations ; but as soon as a significant difference is found there is evidence that the observer or the apparatus is showing signs of wear, and later observations will include a new systematic error. This discussion supposes the normal law to hold, but can obviously be adapted to others.

8. It may appear curious that while I often differ from Eddington, Fisher, and Campbell on fundamental principles, it would only occur rarely that my decision in an individual instance would differ from theirs ; in several cases mentioned above my theory gives Eddington's actual decision, while his own would give the opposite. In such a matter as a dubious harmonic coefficient they would all agree with me and differ from those who think that any such coefficient can be accepted at its face value. I think they would also all agree that the philosophical objections to scientific method, with their over-emphasis of the "excluded middle" and their failure to produce verifiable inferences, are not worth prolonged consideration. The difference is that the theory of probability provides explanations of many steps in the argument, either as inferences from experience or as statements of the fundamental principle that it is possible to learn

* 'Scientific Inference,' top of p. 58 and p. 75.

from experience, that appear to be either arbitrary or additional *a priori* postulates in other methods. My only way of judging other people's mental processes being from their actions, I suspect that when their results do not differ seriously from my own they have been obtained by similar means ; the explanation of the apparent difference in the postulates may then be simply that common-sense principles that appear to me to deserve statement and systematic development are applied by others so easily that they escape recognition. In a sense the theory may be regarded as a contribution to psychology, but it seems that psychology in current use means chiefly the study of the differences between individuals, while the theory of probability concerns mental activities common to all.

XXIX. *The Theory of Electrocapillarity.—IV. The Interpretation of Electrocapillary Data.* By S. R. CRAXFORD, O. GATTY, *and* H. A. C. McKAY †.

Introduction.

THE thermodynamic theory of electrocapillarity has been worked out in the previous papers [1], [2], [3] of this series, and a general electrocapillary equation has been deduced. In the present paper the equation is explained and then applied to special problems that arise in interpreting electrocapillary data with a view to obtaining information about the structure of the double layer. Some of the expressions in this paper have already been obtained by Koenig [4], but he does not treat in any detail the problem of relating the thermodynamic results to the actual experimental data.

The electrocapillary equation is

$$\left\{ \left(\frac{\partial \gamma}{\partial \mathrm{E}} \right)_s \left[1 - \left(\frac{\partial p_1}{\partial \gamma} \right)_s \left(\frac{\partial \mathrm{V}_1}{\partial s} \right)_{p_1} \right] = - \sum_1^c \left(\frac{\partial q_r}{\partial s} \right)_{\mathrm{E}_r} \left(\frac{\partial \mathrm{E}_r}{\partial \mathrm{E}} \right)_s \right\}_{\mathrm{X},\, a,\, \beta - 1}, \quad \cdot \quad \cdot \quad \cdot \quad (1)$$

where

> γ is the surface tension of the interphase between
> phases 1 and 2 ;
>
> s is the area of this interphase, as measured over its
> optical boundary ;
>
> p_1 is the pressure on phase 1, which is the phase
> containing the centre of curvature of the inter-
> phase ;
>
> V_1 is the volume of phase 1 ;
>
> C is the number of chemical components in the
> system (so that owing to the electroneutrality
> condition there are C+1 constituent ions) ;
>
> E_r is defined as $\phi_R - \phi_r$, where ϕ_R is the electrical
> potential of a copper lead from an electrode in
> the system reversible to one of the constituent
> ions R, called the reference ion, and ϕ_r is the
> potential of a copper lead from an electrode
> reversible to one of the other constituent ions, r.
> There is an E_r term associated with each of the
> $1 \ldots r \ldots$ C constituent ions ;
>
> E is any electromotive force associated with the
> system, *i. e.*, any linear combination of the E_r's.
>
> dq_r is an infinitesimal quantity of electricity flowing
> from electrode r through an external circuit on
> to the reference electrode R.

The suffix X denotes (i.) constancy of temperature T
and of the pressure p_2 on phase 2 ; (ii.) that the 12 inter-
phase is the only one whose area alters, *i. e.*, s_k constant—
this will be discussed afresh in paper V. of this series ;
(iii.) that no work is done on the system other than
compressional work at pistons 1 and 2 and electrical work,
i. e., W'' constant. Thus, p_2, T, s_k, and W'' are constant.
The suffix α shows that there are α arbitrary relations
between the extensive variables of the system, and the
suffix $(\beta - 1)$ that there are $(\beta - 1)$ arbitrary relations
between the intensive variables of the system. At
constant s_k and W'' the system has in all C+3 degrees
of freedom, so that $\alpha + \beta = C$. Since two extensive degrees
of freedom are needed to specify the bulks of the two
phases $\alpha \geq 2$, and these α degrees of freedom must be such
as to determine uniquely the extents of both phases.
Finally, $\beta - 1 \geq 0$.

Equation (1) simplifies greatly for an interphase whose

radii of curvature are all great compared with the thickness of the interphase, for the volume correction term on the left-hand side vanishes. If the interphase is very nearly plane constancy of p_2 implies constancy also of p_1, because $p_1 - p_2$ tends to zero. For this case let the suffix X be replaced by X'; X' implies constancy of p_1, p_2, T, s, and W''. Under these conditions, by putting $\alpha = 2$ the $\left(\dfrac{\partial q_r}{\partial s}\right)$ terms on the right-hand side of (1) can be made to refer to surface expansions in which all the intensive variables of the system are kept constant. It is for these expansions only that the $\left(\dfrac{\partial q_r}{\partial s}\right)$ terms can be directly related to the structure of the non-expanding or static interphase. Thus, in applying equation (1) to electro-capillary data X' is put for X, 2 for α, and C—3 for $\beta - 1$. The equation becomes

$$\left[\left(\frac{\partial \gamma}{\partial E}\right)_s = -\sum_1^C \left(\frac{\partial q_r}{\partial s}\right)_{E_r} \left(\frac{\partial E_r}{\partial E}\right)_s\right]_{X', 2, C-3} \quad . \quad (2)$$

The two extensive restrictions are best taken as $dq_1 = dq_2 = 0$; and the C—3 intensive relations, that C—3 linear combinations of the E_r's vanish.

Equation (2) can be slightly extended. In deducing it the flow of electricity in C circuits all directly connected to the reference electrode was considered. Any other set of C independent circuits between the C+1 electrodes would do equally well, provided only that the q and the E in the numerator of each term on the right-hand side always refer to the same circuit.

In paper III. of this series

$$-\left(\frac{\partial q_r}{\partial s}\right)_{E_r,\ X',\ q_1,\ q_2,\ C-3}$$

was denoted by $+\zeta_r{}^{(i)}T_r^*$, where ζ_r is the electrochemical equivalent per gram of ion r, having regard for sign, and the surface adsorption $^{(i)}T_r^*$ is expressed in grams cm.$^{-2}$ (see footnote, p. 362). These units were used in order that the T_r's should be in the same units as the Γ's of Gibbs. In the present paper, which is concerned with the molecular structure of the interphase, it is more convenient to express the T_r's in moles cm.$^{-2}$, so that

$$-\left(\frac{\partial q_r}{\partial s}\right)_{E_r,\ X',\ q_1,\ q_2,\ C-3} \quad \text{is denoted by } z_r F T_r, \text{ where F is}$$

the Faraday and z_r is the valency of the ion r, having regard for sign.

The values of T_r's are independent of the particular set of $(C-3)$ intensive restrictions imposed, because with E_r constant as well during the surface expansion the $\left(\dfrac{\partial q_r}{\partial s}\right)_{E_r}$ refer to expansions with all intensive variables constant. Thus

$$\left[\left(\frac{\partial \gamma}{\partial E}\right)_s = -\sum_3^C \left(\frac{\partial q_r}{\partial s}\right)_{E_r}\left(\frac{\partial E_r}{\partial E}\right)_s\right.$$
$$\left. = +\sum_3^C z_r F T_r \left(\frac{\partial E_r}{\partial E}\right)_s\right]_{X',\, q_1,\, q_2,\, C-3} . \quad . \quad (3)$$

Although the values of the T_r's are independent of the particular choice of the $(C-3)$ intensive variables, $\left(\dfrac{\partial \gamma}{\partial E}\right)_s$ and the $\left(\dfrac{\partial E_r}{\partial E}\right)_s$ are not. Similarly the $\left(\dfrac{\partial \gamma}{\partial E}\right)_s$ and the $\left(\dfrac{\partial E_r}{\partial E}\right)_s$ terms are independent of whether q_1 and q_2 are kept constant or alternative extensive restrictions are imposed, but the $\left(\dfrac{\partial q_r}{\partial s}\right)_{E_r}$ terms are not. It is only at q_1 and q_2 constant that the latter equal $z_r F T_r$.

The relationship of the T_r terms to the structure of the interphase is as follows. Consider a unit area of the interphase and let a normal to the interphase traverse the boundary of this area. Describe in the homogeneous parts of phases 1 and 2 a pair of surfaces such as could be obtained by a normal expansion and contraction of the interphase. These two surfaces and the surface described by the normal enclose an element of volume. Let the molar fractions of the ions in the bulk phases be $^1x_1$, $^1x_2, \ldots {}^1x_C$, ^1x_R in phase 1, and $^2x_1, {}^2x_2, \ldots {}^2x_C$, ^2x_R in phase 2, and let the total numbers of moles in the element of volume in question be $n_1,\ n_2, \ldots n_C,\ n^R$. Then we have a series of $(C+1)$ equations

$$n_r = \lambda_1 {}^1x_r + \lambda_2 {}^2x_r + T_r. \quad . \quad . \quad . \quad (4) \dagger$$

† In paper III. of this series, p. 982, the equation $n_j = \lambda_1 {}^1x_j + \lambda_2 {}^2x_j + {}^{(i)}T_j{}^*$ should read $n_j = \lambda_1 {}^1x_j + \lambda_2 {}^2x_j + {}^{(i)}T_j{}^*/M_j$, where M_j is the molecular weight of ion j. ${}^{(i)}T_j{}^*$ in that paper is in grams-cm.$^{-2}$.

Since $T_1 = T_2 = 0$ by definition, the constants λ_1 and λ_2 can be found from the equations

$$\left. \begin{array}{l} n_1 = \lambda_1{}^1 x_1 + \lambda_2{}^2 x_1, \\ n_2 = \lambda_1{}^1 x_2 + \lambda_2{}^2 x_2, \end{array} \right\} \quad \cdots \quad (5)$$

and then substituted in (4).

The constants λ_1 and λ_2 are measures of the amounts of the two bulk phases included in the element of volume. The first two terms on the right-hand side of each of the equations (4) measure the contributions of the bulk phases to the n's; superposed on these contributions are those due to the surface adsorption terms T_r, which are here expressed to the basis $T_1 = T_2 = 0$. These latter relations may be called " boundary conditions."

The Direct Application of the Electrocapillary Equation.

The whole of the information that can be obtained by differentiating the surface tension once with respect to any E term is contained in a knowledge of the T_r's for all constituent ions under the given conditions; equation (3) contains the complete theory of such differential coefficients. It is of interest to point out that any T_r can usually be obtained from a variety of equivalent equations. Thus in system 1 below T_7 is given by such equations as

$$F T_7 = z_7 F T_7 = \left(\frac{\partial \gamma}{\partial E_7} \right)_{s,\ X',\ q_1,\ q_2,\ E_3,\ E_4,\ E_5,\ E_6}$$

$$= -\left(\frac{\partial \gamma}{\partial E_{67}} \right)_{s,\ X',\ q_1,\ q_2,\ E_3,\ E_{34},\ E_5,\ E_6,}$$

where

$$E_{rs} = E_r - E_s. \quad \cdots \quad \cdots \quad (6)$$

In order to illustrate the scope of the present treatment four systems will be dealt with, and a notation with numerical subscripts for the T_r terms will be defined for each case. The systems are :—

$$(1) \ Hg,\ Tl \ / \ NaCl,\ HCl,\ H_2O,\ EtOH,$$

the interphase being treated as completely polarizable, so that no particle can cross it. This system covers all electrocapillary curves that are obtained by polarizing the interphase.

$$(2) \ Hg,\ Tl \ / \ NaNO_3,\ HNO_3,\ Hg_2(NO_3)_2,\ TlNO_3,$$
$$H_2O,\ EtOH,$$

where the restriction of complete polarizability does not apply. This system covers all cases where the potential across the interphase is controlled by altering the composition of the solution.

$$(3) \ KI, \ CH_3NO_2 \big/ KI, \ H_2O.$$

Here the two solvents are not completely immiscible.

(4) Octyl Alcohol, Benzene / Octyl Alcohol, Water.

Here a capillary active solute is distributed between two

Fig. 1.

SYSTEM 1.
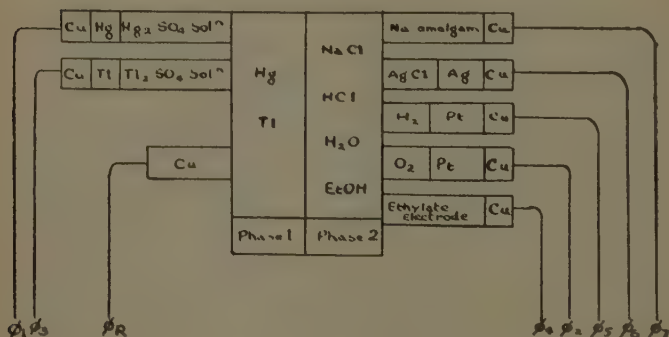
immiscible solvents ; all three components are but negligibly ionized.

Fig. 1 is a diagram of the two phases and the set of eight electrodes. The oxygen electrode is supposed to be reversible to hydroxyl ion, and an ethylate electrode reversible to ethylate ion is also supposed to exist. By definition

$$T_1 = T_2 = 0, \quad . \quad . \quad . \quad . \quad . \quad (7)$$

and from (3)

$$\left(\frac{\partial \gamma}{\partial E_3}\right)_{Y, \ E_4, \ E_5, \ E_6, \ E_7} = z_3 F T_3 = + F T_3, \quad . \quad . \quad (8)$$

$$\left(\frac{\partial \gamma}{\partial E_4}\right)_{Y, \ E_3, \ E_5, \ E_6, \ E_7} = z_4 F T_4 = - F T_4. \quad . \quad . \quad (9)$$

$$\left(\frac{\partial \gamma}{\partial E_5}\right)_{Y,\ E_3,\ E_4,\ E_6,\ E_7} = z_5 F T_5 = +F T_5, \quad . \quad . \quad (10)$$

$$\left(\frac{\partial \gamma}{\partial E_6}\right)_{Y,\ E_3,\ E_4,\ E_5,\ E_7} = z_6 F T_6 = -F T_6, \quad . \quad . \quad (11)$$

$$\left(\frac{\partial \gamma}{\partial E_7}\right)_{Y,\ E_3,\ E_4,\ E_5,\ E_6} = z_7 F T_7 = +F T_7, \quad . \quad (12)$$

where Y includes s, X', q_1, and q_2.

Equation (9) gives the surface adsorption of ethylate ion, T_{EtO^-}, *i. e.*, the amount/cm.^{2} of ethylate ion which would have to be flowed off electrode 4 during a surface expansion with all intensive variables constant. If the alcohol can be supposed to be but negligibly ionized (as may reasonably be assumed under ordinary conditions) every ethylate ion from electrode 4 must combine with a hydrogen ion. It is then legitimate to write

$$T'_{EtOH} = T_{EtO^-} \quad \text{and} \quad T'_{H^+} = [T_{H^+} - T_{EtO^-}]$$

and to work with T'_{EtOH} and T'_{H^+} instead of T_{EtO^-} and T_{H^+}.

This can be shown rigorously by using a new set of circuits between the eight electrodes. There are used 1—R, 2—R, 3—R, 5—R, 6—R, and 7—R as before, but 4—5 instead of 4—R. Surface adsorption terms calculated on the new basis will be dashed (T_1' etc.). dq_{45} will be taken as positive when it refers to external transfer of positive charge on to the hydrogen electrode, and z_{45} will be taken as -1 to make T'_{45} comparable to T terms and to the other T' terms. As before, T_1' and T_2' are taken as zero. Equations (8), (10), (11), and (12) then hold with E_{45} in place of E_4, and a T' term in place of the T term ; (8), for instance, becomes

$$\left(\frac{\partial \gamma}{\partial E_3}\right)_{Y,\ E_{45},\ E_5,\ E_6,\ E_7} = +z_3 F T_3' = +F T_3'. \quad (13)$$

In place of (9) there is a new equation

$$\left(\frac{\partial \gamma}{\partial E_{45}}\right)_{Y,\ E_3,\ E_5,\ E_6,\ E_7} = +z_{45} F T'_{45} = -F T'_{45}. \quad (14)$$

It follows from (6) that the right-hand side of (8) is

identical with that of (13) and the right-hand side of (9) with that of (14).   Hence

$$T_3 = T_3',$$
$$T_4 = T'_{45}, \quad \cdots \cdots \quad (15)$$

and similarly

$$T_6 = T_6',$$
$$T_7 = T_7'.$$

Again, from the identity

$$\left(\frac{\partial \gamma}{\partial E_5}\right)_{ZE_{45}} = \left(\frac{\partial \gamma}{\partial E_5}\right)_{ZE_4} + \left(\frac{\partial \gamma}{\partial E_4}\right)_{ZE_5}\left(\frac{\partial E_4}{\partial E_5}\right)_{ZE_{45}},$$

where Z implies constancy of s, X', q_1, q_2, E_3, E_6, and E_7, it may be shown that

$$z_5 T_5' = z_5 T_5 + z_4 T_4;$$
$$\therefore \quad T_5' = T_5 - T_4, \quad \cdots \cdots \quad (16)$$

(15) and (16) are the equations required.

Another application of interest arises when the C—3 intensive restrictions are $dE_3 = 0$ and $dE_4 = dE_5 = dE_6 = dE_7 = dE *$ (say).   Equation (3) then becomes

$$\left(\frac{\partial \gamma}{\partial E*}\right)_{Y, E_3, E_{45}, E_{56}, E_{67}} = \sum_{r=4}^{7} z_r F T_r = F(-T_4 + T_5 - T_6 + T_7)$$
$$\cdots \quad (17)$$

The right-hand side of this equation represents the total electric change flowing out of electrodes 4, 5, 6, and 7 during a surface expansion under appropriate conditions, *i. e.*, the total charge flowing away from phase 2.   From the condition for electrical neutrality this must be equal to the total charge flowing into phase 1 through electrodes R and 3.

The electroneutrality condition is

$$\sum_{1}^{C} z_r T_r + z_R T_R = 0,$$

so that from (17)

$$\left(\frac{\partial \gamma}{\partial E*}\right)_{Y, E_3, E_{45}, E_{56}, E_{67}} = -z_3 F T_3 - z_R F T_R = F(-T_3 + T_R).$$
$$\cdots \quad (18)$$

Fig. 2.

SYSTEM 2
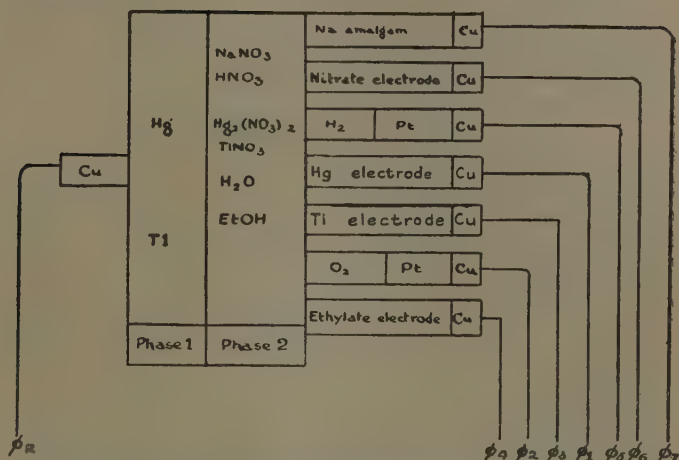
For this system all the equations (7) to (18) are valid as for system 1; the subscript 6 now refers to the nitrate ion instead of the chloride ion. The right-hand side of (17) no longer represents the total charge flowing out of phase 2, so (17) and (18) lose their special interest. They can be replaced by a new equation, which holds for system 1 also. If $d\mathrm{E}_3 = d\mathrm{E}_4 = d\mathrm{E}_5 = d\mathrm{E}_6 = d\mathrm{E}_7 = d\mathrm{E}^*$, the electrocapillary equation gives

$$\left(\frac{\partial \gamma_0}{\partial \mathrm{E}^*} \right)_{\mathrm{Y},\ \mathrm{E}_{34},\ \mathrm{E}_{45},\ \mathrm{E}_{56},\ \mathrm{E}_{67}} = + \sum_{1}^{C} z_r \mathrm{F} \varGamma_r = -z_\mathrm{R} \mathrm{F} \varGamma_\mathrm{R}. \quad (19)$$

Fig. 3.

SYSTEM 3.
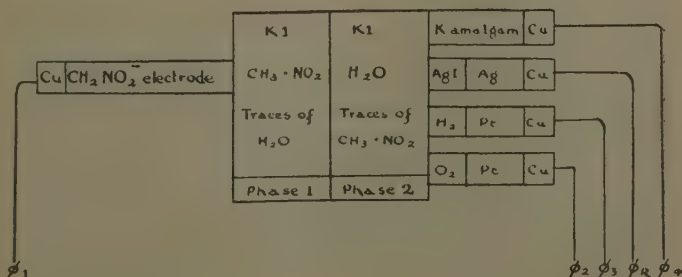
The most convenient set of circuits to use is $1-3$, $2-3$, $3-R$, and $4-R$; the T terms are calculated to the basis

$$T_{13} = T_{23} = 0. \quad . \quad . \quad . \quad . \quad . \quad (20)$$

The electrocapillary equation then gives

$$\left(\frac{\partial \gamma}{\partial E_3} \right)_{s,\, X',\, q_{13},\, q_{23},\, E_4} = +z_3 F T_3 = +F T_3, \quad . \quad (21)$$

$$\left(\frac{\partial \gamma}{\partial E_4} \right)_{s,\, X',\, q_{13},\, q_{23},\, E_3} = +z_4 F T_4 = +F T_4, \quad . \quad (22)$$

$$\left(\frac{\partial \gamma}{\partial E_4} \right)_{s,\, X',\, q_{13},\, q_{23},\, E_{34}} = +z_3 F T_3 + z_4 F T_4,$$
$$= -z_R F T_R = +F T_R. \quad . \quad (23)$$

System 4.

This system is best dealt with by the methods of paper II. of this series rather than those of paper III. Let 1 be water, 2 be benzene, and 3 be octyl alcohol. Then from equation (17) of paper II., neglecting the volume correction term,

$$\left(\frac{\partial \bar{\gamma}}{\partial \bar{F}_3} \right)_{s,\, X',\, N_1,\, N_2} = -T_3 \quad . \quad . \quad . \quad (24)$$

for the conditions

$$T_1 = T_2 = 0. \quad . \quad . \quad . \quad . \quad (25)$$

The Special Properties of a Completely Polarizable Interphase.

The most important type of system to be dealt with is one containing two phases separated by a completely polarizable interphase. Let phase 1 contain the ions R, 1, 3 ... C', all other constituent ions of the system being supposed to be at a negligible concentration in this phase. Similarly let phase 2 contain ions 2, C'+1, ... C. Ions 1 and 2 will be chosen to determine the extents of the two phases, dq_1 and dq_2 being made to vanish. (It may be helpful to visualize phase 1 as metallic, phase 2 as a solution, and the reference ions

as electrons.) In consequence of the restriction of complete polarizability no particle will cross the interphase between phases 1 and 2.

Now let a change be made in the surface tension subject to the conditions that s, X', q_1, q_2, E_3, E_4, ... $E_{C'}$ are constant and that

$$dE_{C'+1} = dE_{C'+2} = \ldots dE_C = dE^* \quad \text{(say)};$$

dE^* is a change in electromotive force of special significance. It is in the first place equal to the change in electromotive force in any circuit connecting an electrode in phase 1 with an electrode in phase 2. E^* may then be split up into the sum of three or more interfacial potentials: $^1\varDelta^2\phi$ across the interphase itself and two solution-electrode surfaces involving at least two interfacial potential differences.

The conditions imposed on the system are such as ensure constant composition of both bulk phases : for instance, in system 1 above constant E_{67} implies constant concentration of sodium chloride. Consequently the solution-electrode interfacial potential differences must be constant, and

$$dE^* = d^1\varDelta^2\phi.$$

It is only for the special case of a completely polarizable interphase that dE^* has this special significance.

The first differential of the surface tension with respect to E^* also has a special significance. The electrocapillary equation gives

$$\left(\frac{\partial \gamma}{\partial E^*}\right)_{Y,\, E_3 \ldots E_{C'},\, E_{(C'+1)C} \ldots E_{(C-1)C}} = +F \sum_{C'+1}^{C} z_r T_r$$
$$= -F\left(\sum_{3}^{C'} z_r T_r - z_R T_R\right)$$
$$= -Q, \quad \ldots \quad (26)$$

where Y includes s, X', q_1, and q_2, as before, $E_{(C'+1)C} = E_{(C'+1)} - E_C$ etc., and Q is the net total electric charge per unit area of the interphase due to the constituent ions of phase 1. Q is called the charge on the double layer.

If it is further postulated that there is one unique boundary in the completely polarizable interphase that no particle can cross, rather than a series of such planes,

one for each ionic species, the double layer may be simply illustrated :—

Fig. 4.

| Phase 1 | +Q | −Q | Phase 2 |

Impenetrable Boundary.
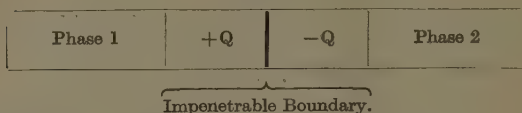
Following v. Helmholtz [5] it is possible to consider the double layer in the case of a polarized interphase as a simple electrostatic condenser, and to calculate its capacity per unit area, C, from

$$C = \left[\frac{\partial Q}{\partial E^*} = -\frac{\partial^2 \gamma}{\partial E^{*2}}\right]_{Y, E_3 \ldots E_{C'}, E_{(C'+1)C} \ldots E_{(C-1)C}} \quad . \; (27)$$

Now the capacity per unit area of a parallel plate con-denser is given by

$$C = \frac{D}{4\pi d},$$

where D is the dielectric constant of the intervening medium and d is the distance between the " plates " ; hence it is possible to calculate values of D/d. The results of such calculations will be considered in a later section.

Q is equal to the net electric charge carried by all the constituent ions of phase 1 contained in a volume element comprising portions of phases 1 and 2 and unit area of the interphase. It must have a value independent of the total quantity of phase 1 present in the element considered, since the bulk parts of the phases, which are electrically conducting media, must be electrically neutral. Thus the value of Q, unlike the values of the individual T_r terms, is independent of the particular choice of extensive restrictions, *i. e.*, of which particular two ions are labelled 1 and 2, and for which T_1 and T_2 are taken as zero. Thus Q, and hence D/d, are properties of a completely polarizable interphase independent of the " choice of boundaries," as the process of fixing two T_r terms may be called by analogy with Gibbs's procedure where one Γ_r term is made to vanish by the choice of a special boundary.

In the non-polarized case the left-hand side of equation (26) can still be calculated, but neither it nor $d\mathrm{E}^*$ has the same electrostatic significance as for the polarized case. The polarized case must, however, actually be a limiting case of the non-polarized case, and it should be possible to link up the two cases continuously. The way to do this would be to obtain experimentally the values of the T_r's and the various $\dfrac{\partial T_r}{\partial \mathrm{E}}$ terms for the non-polarized case and to construct an interphase equation from them. Then the observed relations would be extrapolated to zero concentration of each of the ions in one phase or other. An estimate of the errors involved in assuming complete polarizability might be obtained in this way.

The Solution-Mercury Interphase as a completely Polarizable Interphase.

Over a wide range of potential the interphase between mercury and a suitable electrolytic solution can be taken as completely polarizable. For instance, with $N/1$ KNO_3 aq. continuous electrolysis is negligible throughout the range $E_{NCal.} = 0$ to $E_{NCal.} = -1\cdot2$ volts. Throughout this range the mercury is too negative for mercurous ions to be electrolyzed into the solution to form mercury salts and too positive for cations from the solution to be discharged on it at appreciable rates; moreover mercury has too high a hydrogen overvoltage for appreciable evolution of hydrogen to occur.

This statement is proved by the fact that the observed density of the depolarization current over this range of potential in the capillary electrometer is small and of the order of 10^{-3} to 10^{-4} amp. cm.$^{-2}$. This is confirmed by the behaviour of the meniscus in a capillary electrometer. When the meniscus is displaced, and hence its area and the interfacial potential difference altered on open circuit, it is only with extreme slowness that the mercury returns to its original position, whereas on closed circuit it returns immediately (Lippmann [6]). In the first case the potential can return to its original value only by the passage of ions across the interphase; Lippmann's experiment shows that this process is very slow compared with adjustments of potential through an external circuit.

The only interfacial reaction that occurs under the conditions without the flow of a depolarizing current is attack of the metal by dissolved oxygen †; the rate of this reaction is small and can be reduced almost to zero in carefully prepared oxygen-free solutions. The elimination of oxygen has in point of fact little effect on electrocapillary curves. Hence it appears that, in the potential ranges indicated, the solution-mercury interphase approximates closely to an interphase containing a boundary that no charged particle can cross, *i. e.*, to a completely polarizable interphase, and, further, that this holds as far as electrocapillary data are concerned both in aerated and air-free solutions.

Koenig [7] has shown directly that the small residual current in the capillary electrometer is of no consequence. He made small additions of mercurous nitrate to aqueous potassium nitrate solutions, and thereby increased the depolarization current from $2 \cdot 10^{-10}$ to $4 \cdot 10^{-10}$ amps. He found that for $M/1$ KNO_3 the electrocapillary curve is unchanged, and for $M/10$ KNO_3 it is only slightly displaced.

The Electrostatic Capacity of the Double Layer.

Further evidence in favour of the substantially complete polarizability of the interface is afforded by the agreement of $\left(\dfrac{\partial \gamma}{\partial \mathrm{E}}\right)_s$, obtained from the electrocapillary curve, with $-\left(\dfrac{\partial q}{\partial s}\right)_\blacksquare$ for the same potential, as measured directly with a dropping mercury electrode. The latter gives the charge per square centimetre that has to be flowed on to an expanding interface to maintain it at constant potential. It is only for a completely polarizable interphase that the Q of equation (26) can be identified with $\left(\dfrac{\partial q}{\partial s}\right)_\mathrm{E}$ measured in this way, which should therefore vary only slightly with dropping rate for such interphases, as is indeed found to be the case.

A comparison of these two quantities has been made for NaCl and HCl solutions at a series of concentrations

† Conversion of H_2 to $2H^+$ is very slow compared to the rate of attack by O_2 even at high ratios of the partial pressures of hydrogen to oxygen gas over the solution.

and over most of the available potential range ; the values of $\left(\dfrac{\partial \gamma}{\partial \mathrm{E}}\right)_s$ obtained from the electrocapillary measurements of Craxford [8] agree with those of $-\left(\dfrac{\partial q}{\partial s}\right)_{\mathrm{E}}$ obtained directly from the dropping electrode experiments of Philpot [9]. Frumkin [10] has made a similar comparison, and has also compared the potential of the electrocapillary maximum with the potential at which $\left(\dfrac{\partial q}{\partial s}\right)_{\mathrm{E}}$ vanishes in a number of instances ; he has found good agreement even when the electrocapillary curve is strongly distorted from the simple parabolic form. Philpot's dropping electrode results are actually some 20 per cent. higher than Craxford's electrocapillary results. This is probably due in the main to two things—first, Philpot applied a correction, not applied by Craxford, increasing his figures by about 10 per cent., and secondly, in calculating the rate of increase in area of his mercury surface Philpot assumed that his mercury drops were spherical. Any deviation from sphericity would make the apparent capacity too high, for a sphere has a smaller surface : volume ratio than any other three-dimensional form. Frumkin's work was probably free from such error because his drops were very small.

Although there is agreement between the results for the charge of the double layer obtained with the dropping electrode and with the capillary electrometer, the results are in disagreement with another series of measurements, namely, those of Bowden and Rideal [11] and of Erdey-Gruz and Kromrey [12]. These authors measured $\dfrac{1}{s}\left(\dfrac{\partial q}{\partial \mathrm{E}}\right)_s$ directly by flowing charge on to a stationary interphase and observing the resulting change of potential across it. Now although

$$\frac{1}{s}\left(\frac{\partial q}{\partial \mathrm{E}}\right)_s = \left(\frac{\partial}{\partial s}\right)_{\mathrm{E}}\left(\frac{\partial q}{\partial \mathrm{E}}\right)_s = \left(\frac{\partial}{\partial \mathrm{E}}\right)_s\left(\frac{\partial q}{\partial s}\right)_{\mathrm{E}},$$

their results for the capacity of the interphase as given by $\dfrac{1}{s}\left(\dfrac{\partial q}{\partial \mathrm{E}}\right)_s$ are three or more times smaller than the

corresponding capacities as given by $\left(\dfrac{\partial}{\partial \mathrm{E}}\right)_s \left(\dfrac{\partial q}{\partial s}\right)_{\mathrm{E}}$ obtained from dropping electrode or electrocapillary data.

This discrepancy has recently been cleared up by Proskurnin and Frumkin [13]. They showed that a stationary mercury surface is very susceptible to contamination by grease and similar substances. They took great care to avoid contamination—for instance, none of their taps were greased. The interphase was cleaned at the outset by having the mercury in a glass cup which could be filled from underneath, so that mercury overflowed over the rim of the cup. Apart from this their method was essentially that of Erdey-Gruz and Kromrey. The results obtained agreed with those obtained by electrocapillary and dropping electrode measurements. Touching the mercury surface with a stick of picein was, however, sufficient to produce a much lower capacity, so, since Erdey-Gruz and Kromrey used picein in the interior of their cell, there can be little doubt that they were dealing with a contaminated interphase, as Erdey-Gruz himself has since admitted. Whether a similar or another explanation holds for the work of Bowden and Rideal is still open to doubt. The present authors, who have benefited by discussing the matter with Dr. Bowden, think that the higher value for the capacity represents the true value, since this agrees with results obtained from the capillary electrometer which represents a system more nearly in equilibrium ; but judgment as to the explanation of the low capacities still obtained by Dr. Bowden and his co-workers must be postponed till more evidence is available.

For appropriate solutions and potentials it may therefore be assumed that it is justifiable to treat the solution-mercury interphase as completely polarizable, and to apply equations (26) and (27) to calculate the charge and capacity of the double layer no matter what the shape of the electrocapillary curve.

Electrocapillary Curves of Salt Solutions against Mercury.

A system consisting of an ordinary salt solution, containing no non-electrolyte other than the solvent itself and no dischargeable ion, and a pure mercury phase

can be dealt with as a special case of system 1 above. Electrodes 3 and 4 are not needed and are omitted. The rest of the electrodes are most conveniently connected by the set of circuits 1—R, 5—R, 6—R, 7—R, and 2—5. Then, calculating surface adsorptions to the basis

$$T_1 = T_{25} = 0 \quad \text{. . . . . . . (28)}$$

the electrocapillary equation gives

$$\left(\frac{\partial \gamma}{\partial E_5}\right)_{Y, E_6, E_7} = z_5 F T_5, \quad \text{. . . . . (29)}$$

$$\left(\frac{\partial \gamma}{\partial E_6}\right)_{Y, E_5, E_7} = z_6 F T_6, \quad \text{. . . . . (30)}$$

$$\left(\frac{\partial \gamma}{\partial E_7}\right)_{Y, E_5, E_6} = z_7 F T_7, \quad \text{. . . . . (31)}$$

$$\left(\frac{\partial \gamma}{\partial E^*}\right)_{Y, E_5, E_{67}} = z_6 F T_6 + z_7 F T_7, \quad \text{. . (32)}$$

where Y implies constancy of s, X′, q_1, and q_{25}, and E* in equation (32) is either E_6 or E_7. When T_5 is negligible the right-hand side of (32) is equal to $-Q$.

The Approximations necessary for Interpreting Existing Electrocapillary Data †.

Since $dq_1 = dq_{25} = 0$, circuits 1—R and 2—5 can be omitted. But the three circuits 5—R, 6—R, and 7—R are still left, whereas in practice an electrocapillary curve is obtained using only one circuit, say 6—R, between the two phases.

Circuit 5—R can be omitted if the differentiations are carried out at $dq_5 = 0$ instead of $dE_5 = 0$; this is usually feasible in neutral solution, neutral being understood in the general sense that the solvent ions are present in equivalent amounts. This alteration must necessarily mean that in the corresponding surface expansion intensive quantities are allowed to vary, so that the $\left(\frac{\partial \gamma}{\partial E}\right)_s$ terms do not give true T^* terms (paper III., p. 980). The errors involved are given by the identity

$$\left(\frac{\partial \gamma}{\partial E_r}\right)_{Z, q_5} = \left(\frac{\partial \gamma}{\partial E_r}\right)_{Z, E_5} + \left(\frac{\partial \gamma}{\partial E_5}\right)_{Z, E_r}\left(\frac{\partial E_5}{\partial E_r}\right)_{Z, q_5},$$

† See note added in proof, p. 400.

which becomes

$$\left(\frac{\partial \gamma}{\partial E_r}\right)_{Z,\, q_5} = z_r F T_r + z_5 F T_5 \left(\frac{\partial E_5}{\partial E_r}\right)_{Z,\, q_5} \quad . \quad . \quad (33)$$

when Z comprises an appropriate set of variables. Since neither T_5/T_r nor $\left(\dfrac{\partial E_5}{\partial E_r}\right)_{Z,\, q_5}$ can be very much greater (numerically) than unity, either of the conditions

$$\left.\begin{array}{c} |\,T_5\,| << |\,T_r\,| \\ \left|\left(\dfrac{\partial E_5}{\partial E_r}\right)_{Z,\, q_5}\right| << 1 \end{array}\right\} \quad . \quad . \quad . \quad . \quad (34)$$

is sufficient to make the replacement of E_5 by q_5 in the conditions of constancy, a valid approximation.

In neutral aqueous solution the approximation is justifiable on both theoretical and practical grounds. Unless one of the solvent ions is particularly strongly adsorbable at the interphase the low concentration of these ions ensures that the correction term in (33) is negligible. Both ions must be considered, for strong positive adsorption of the hydroxyl ion would, in the system of T terms adopted here, be represented by a large negative value of T_5.

A sufficiently low concentration of solvent ions ensures that both the conditions (34) are fulfilled. In the first place T_5 must vanish altogether in the limit when ion 5 is at zero concentration, though the concentration at which T_5 becomes negligible may be very low if either solvent ion is strongly specifically adsorbed. In the second place it is evident that E_5, the potential of a hydrogen electrode in the solution, cannot be appreciably altered by flowing charge in the two remaining circuits 6—R and 7—R, whereas both E_6 and E_7 can be changed considerably. Low adsorbability of the solvent ions is again necessary to ensure that the limiting concentration for the validity of the condition in question is not excessively low. As regards aqueous solutions electro-capillary curves for acids and bases show that the hydrogen ion is no more adsorbable than other elementary cations. The hydroxyl ion is more adsorbable, but it seems that concentrations of the order of 10^{-6} or 10^{-7} are quite low enough for (34) to hold.

It is valid then to put E_5 in place of q_5 in each of equa-

tions (30), (31), and (32) provided that the solution is neutral ; the equations become

$$\left(\frac{\partial \gamma}{\partial E_6}\right)_{Y,\, q_5\, E_7} = z_6 F \mathcal{T}_6, \quad \ldots \quad \ldots \quad (35)$$

$$\left(\frac{\partial \gamma}{\partial E_7}\right)_{Y,\, q_5, E_6} = z_7 F \mathcal{T}_7, \quad \ldots \quad \ldots \quad (36)$$

$$\left(\frac{\partial \gamma}{\partial E^*}\right)_{Y,\, q_5,\, E_{67}} = z_6 F \mathcal{T}_6 + z_7 F \mathcal{T}_7. \quad \ldots \quad (37)$$

For salt solutions containing free acid or alkali the approximation breaks down. For solutions of pure acids or alkalis (*i. e.*, in general solutions containing only one ion other than the solvent ions), however, the necessity for an approximation on account of adsorption of solvent ions does not arise, since for such solutions one of the circuits 6—R and 7—R becomes unnecessary and can be omitted. Thus for a solution of HCl circuit 7—R is omitted, and we have simply the equations

$$\left(\frac{\partial \gamma}{\partial E_5}\right)_{Y,\, E_6} = z_5 F \mathcal{T}_5, \quad \ldots \quad \ldots \quad (38)$$

$$\left(\frac{\partial \gamma}{\partial E_6}\right)_{Y,\, E_5} = z_6 F \mathcal{T}_6, \quad \ldots \quad \ldots \quad (39)$$

$$\left(\frac{\partial \gamma}{\partial E^*}\right)_{Y,\, E_{56}} = z_5 F \mathcal{T}_5 + z_6 F \mathcal{T}_6. \quad \ldots \quad (40)$$

where Y includes s, X', q_1, and q_{25} as before, and E* is either E_5 or E_6.

A second approximation must now be applied to equation (37). In practice, at constant concentration of salt, the value of $\left(\dfrac{\partial \gamma}{\partial E^*}\right)$ is found at $dq_7 = 0$ instead of $dE_{67} = 0$; circuit 7—R is, in fact, omitted. This substitution is valid provided

$$\left[\left(\frac{\partial \gamma}{\partial E_{67}}\right)_{E_6}\left(\frac{\partial E_{67}}{\partial E_6}\right)_{q_7}\right]_{Y,\, q_5}$$

is small enough. The $\left(\dfrac{\partial \gamma}{\partial E_{67}}\right)_{Y,\, q_5,\, E_6}$ is of the same order of magnitude as the $z_r F \mathcal{T}_r$ terms, so it is sufficient that

$\left(\dfrac{\partial E_{67}}{\partial E_6}\right)_{Y,\,q_5,\,q_7}$ should be numerically small. This is the

case, for it is impossible to alter E_{67} appreciably by flow of charge in the one remaining circuit, $6-R$, whereas dE_6 can be altered considerably by this means. This approximation would break down only in the case of a salt with an exceedingly strongly adsorbed ion at very low concentration.

The final equation is thus

$$\left(\frac{\partial \gamma}{\partial E_6}\right)_{s,\,X',\,q_1,\,q_{25},\,q_5,\,q_7} = z_6 F T_6 + z_7 F T_7$$
$$= -Q. \quad . \quad . \quad . \quad . \quad (41)$$

Equation (40) yields a similar equation, since E_{56} can be replaced by q_5 for the same reason that E_{67} was replaced by q_7.

It is interesting to note that, according to Frumkin and Gorodetzkaja [14], hydroxyl ion is strongly adsorbed at a solution-gallium interphase. It may not, therefore, be justifiable to replace E_5 by q_5 in this case.

The Capacities of the Ions in the Double Layer.

The charge-potential curves for aqueous solutions of many inorganic electrolytes usually show two nearly linear regions, separated by an exponential region in the neighbourhood of the electrocapillary maximum. This is true for the differentials of Koenig's and Frumkin's [15] electrocapillary curves for potassium nitrate and of Craxford's [8] curves for several inorganic salts, and also for Philpot's [9] dropping-electrode curves for sodium and hydrogen chlorides. Linear regions are observed, too, for the grease-contaminated surfaces investigated by Bowden and Rideal [11] and Erdey-Gruz and Kromrey [12]. This indicates that away from the maximum the interphase is behaving essentially like a parallel plate condenser (see v. Helmholtz [5]). Moreover the primary effect of a grease film seems to correspond to nothing more fundamental than the insertion of a dielectric between the plates.

In the simple original theory of v. Helmholtz, C was assumed to be constant over the whole electrocapillary curve, so that integration of (27) predicted that the curve

should be a parabola with its axis parallel to the axis of surface tension ; since C is positive, the curve should exhibit a maximum in the surface tension. Actually, as just stated, Q is not strictly a linear function of E*, so the original theory was evidently too simple. The theory suffered an eclipse when the non-parabolic nature of many electrocapillary curves was discovered ; but since many of these curves consist of two parabolic branches united through a small non-parabolic region round the maximum the chief modification necessary is simply to give C different values on the two branches.

The next theory was the diffuse layer theory of Gouy [16]. He considered that thermal agitation would break up a rigid Helmholtz double layer, so that the excess of charge on a phase would be distributed at the interphase according to Maxwell-Boltzmann statistics. Near the interphase there is supposed to be an excess of charge of one sign or the other, and this excess becomes less at greater distances from the interphase. This theory leads to various difficulties : the worst is that over 90 per cent. of the ions would have to lie far closer to the interphase than the ionic radius. This shows itself up in the fact that the capacities calculated from the theory are about ten times as great as those obtained directly from experiment.

Stern [17] pointed out how this difficulty arose from a neglect of the finite size of the ions, and suggested that the actual state of affairs is best represented by a rigid Helmholtz layer with a diffuse layer outside it. His calculations predict that the layer should be predominantly diffuse at potentials near the electrocapillary maximum and predominantly of the Helmholtz type at potentials removed from the maximum. The charge-potential curves should consist of two straight lines joined by an exponential region through the maximum, a prediction that has been verified for solutions of NaCl and HCl by Philpot [9]. Away from the maximum departures from linearity do sometimes occur in differentiated electrocapillary curves ; these will be discussed later. Meanwhile there is in general every reason for taking the values of C on the two branches, usually called the capacities of the ions, as a basis for discussion.

The capacities of a number of ions in the aqueous solution-mercury interphase have been measured by Craxford, and are given in Table I.

It is a remarkable and unexplained fact that all ordinary inorganic cations have the same capacity, irrespective of size or valency; even the hydrion has the same capacity as other cations. (Some organic cations such as tetraethylammonium [18] have, however, higher capacities

TABLE I.

Ion.	Capacity in mfd./cm.³
H^+	19·0
Na^+	19·2
K^+	19·3
Ca^{++}	19·1
Al^{+++}	19·0
NO_3^-	23·8
ClO_4^-	25·5
SO_4^{--}	40·4
Cl^-	43·0
CNS^-	52·7
Br^-	92·5
I^-	160

TABLE II.

Solvent.	Capacity in mfd./cm.²
Methyl alcohol	12·8
Ethyl alcohol	11·5
Acetone	9·6
Pyridine	10·8
(Water	19·1)

than the normal.) This holds true in other solvents than water; Frumkin's cation capacities in four non-aqueous solvents are listed in Table II.

McKay [19] has obtained confirmatory evidence that lithium, sodium, and calcium ions all have the same capacity in ethyl alcohol, the figure being much the same as Frumkin's.

The anion capacities vary a great deal. Not all anions give straight-line charge-potential curves, so that it is not always possible to give a definite value for the capacity, since it is a function of the potential. It is evident in such cases that the simple Helmholtz picture is breaking down; the phenomenon will be discussed later. The curvature of the charge-potential curve means that the capacity quoted for the iodide ion, and possibly also that for the bromide ion, is only an average value over the positive branch of the curve; it becomes impossible, too, to give a value for the capacity of the sulphide ion or for almost any anion in a non-aqueous solvent.

If D is taken as unity and C as 20 mfd./cm.² in the expression

$$C = \frac{D}{4\pi d}$$

for the capacity of a parallel plate condenser, the value of d comes out at 0·5 Ångström units; this is smaller than an ionic radius. It is probable, therefore, both for this reason and on general grounds, that the ions in the double layer are considerably deformed in such a way as to reduce the distance between the "plates." The capacities of the anions do indeed roughly follow the order of deformabilities as given by refractivity data[20]. Such divergences as do exist do not necessarily show this view to be false; there are, for instance, possible effects due to solvation of the ions, and to the fact that refractivity data do not give directly values for the polarizability at zero frequency. But the difficulty of the constancy of cation capacities still remains.

A second reason why the values of D/d should be unexpectedly high is that the dielectric constant of the solvent must be taken into account. The experimental results show that the solvent has a considerable influence on the capacities of cations in the sense that a lower dielectric constant produces a smaller capacity. The relative magnitude of the figures in Table II. would indeed be given roughly by taking for D the bulk dielectric constant of the solvent. The solvent might affect the capacity of the double layer in a variety of ways :—

(*a*) Even if the ions are in direct contact with the mercury the lines of electrostatic forces between the

ions and the mercury will be partially deflected so as to pass through a certain number of solvent molecules. This may have a considerable effect, because the number of ions in the double layer is very much fewer than the number required to form a unimolecular layer [15], so that each ion in the rigid layer is for the most part surrounded by solvent molecules.

(b) The use of the macroscopic dielectric constant of the pure solvent in the discussion of electrocapillary problems is liable to be wrong, because the solvent cannot be treated as a continuous medium ; local electrostriction and dielectric saturation may play important parts in affecting the properties of the solvent in the immediate neighbourhood of the interphase. Indeed, since single interphase potential differences have no physical significance, all the short-range forces which invalidate Born's equation for the energy of ion solvation [21] may be supposed to have some effect on the energy required to bring an electric charge, and therefore an ion, into the double layer. Changes would arise in the observed potential difference corresponding to changes in this energy.

(c) The ions are probably more or less solvated, and may be separated from the metal by one or more solvent molecules.

Dilution Shifts : the Standard Shift.

Altering the concentration of the dissolved salt causes changes in both the electrocapillary and charge-potential curves. The effect is best treated as a variation of E_{67}, for we have the relation

$$dE_{67} = \frac{+z_6 - z_7}{z_6 z_7} \cdot \frac{RT}{F} d\ln a_{67},$$

where a_{67} is the mean ionic activity coefficient of the salt in the solution.

For the moment let it be assumed that measurements of potential are made against electrode 6 throughout the electrocapillary experiments. Then the vertical displacement of the electrocapillary curve is given by

$$\left(\frac{\partial \gamma}{\partial E_{67}}\right)_{Y, \, q_6, \, E_6}.$$

Now $[dE_{67} = -dE_7]_{E_6}$, so from (36)

$$\left(\frac{\partial \gamma}{\partial E_{67}}\right)_{Y, q_5, E_6} = -z_7 F T_7. \quad . \quad . \quad . \quad (42)$$

The horizontal displacement of the curve is given by

$$\left(\frac{\partial E_6}{\partial E_{67}}\right)_{Y, q_5, \gamma} = -\left[\left(\frac{\partial \gamma}{\partial E_{67}}\right)_{E_6} \middle/ \left(\frac{\partial \gamma}{\partial E_6}\right)_{E_{67}}\right]_{Y, q_5}$$

$$= -\frac{z_7 F T_7}{Q}, \quad . \quad . \quad . \quad . \quad . \quad (43)$$

using (37) and (42). It is important to realize that expression (42) contains no information that cannot be obtained equally well from the slope of the electrocapillary curve together with data for expression (43); it is therefore sufficient to consider only the horizontal shift of the curve on dilution.

The vertical shift of the charge-potential curve is given by

$$\left(\frac{\partial Q}{\partial E_{67}}\right)_{Y, q_5, E_6} = \left(\frac{\partial^2 \gamma}{\partial E_{67} E_6}\right)_{Y, q_5}$$

$$= z_7 F \left(\frac{\partial T_7}{\partial E_6}\right)_{Y, q_5, E_{67}},$$

using (37) with $E^* = E_6$, and (42); the result is of no particular interest. The horizontal shift is more important; it is given by

$$\left(\frac{\partial E_6}{\partial E_{67}}\right)_{Y, q_5, Q} = -\left(\frac{\partial E_6}{\partial Q}\right)_{Y, q_5, E_{67}} \left(\frac{\partial Q}{\partial E_{67}}\right)_{Y, q_5, E_6}$$

$$= -z_7 F \left(\frac{\partial T_7}{\partial Q}\right)_{Y, q_5, E_{67}}. \quad . \quad . \quad . \quad (44)$$

The vertical displacement of the electrocapillary maximum with concentration is given by

$$\left[\left(\frac{\partial \gamma}{\partial E_{67}}\right)_{Q=0} = \left(\frac{\partial \gamma}{\partial E_{67}}\right)_{E_6} + \left(\frac{\partial \gamma}{\partial E_6}\right)_{E_{67}} \left(\frac{\partial E_6}{\partial E_{67}}\right)_{Q=0}\right.$$

$$= \left. -z_7 F T_7 - z_7 F Q \left(\frac{\partial T_7}{\partial Q}\right)_{E_{67}}\right]_{Y, q_5},$$

using (37), (42), and (44). Hence

$$\left(\frac{\partial \gamma}{\partial E_{67}}\right)_{Y, q_5, Q=0} = -z_7 F T_7. \quad . \quad . \quad (45)$$

The equation for the horizontal shift is the same as (44), which does not simplify at all at the electrocapillary maximum.

It has so far been supposed that electrode 6 has been used as the measuring electrode. This corresponds to the experimental arrangement used by Philpot, but the usual method is to make all measurements against a standard half-cell, usually a normal or a saturated calomel electrode. Let the electrical potential of a copper lead from the reference electrode R, less the electrical potential of a copper lead from such a half-cell, be denoted by $E_{Cal.}$. Then $E_{Cal.} - E_6$ is equal to the electromotive force of the cell

Standard half-cell	Half-cell solution	Solution under investigation	Electrode 6 (reversible to Cl^-).

This cell involves a liquid junction of unspecified form, so a rigorous thermodynamic treatment is hardly possible. Provided both solutions are in the same solvent, however, its electromotive force is given sufficiently exactly by

$$E_0 - \frac{RT}{z_s F} ln a_s + \frac{RT}{z_6 F} ln a_{67} + \Delta\psi,$$

where E_0 is the difference between the standard electrode potentials of the two electrodes in the cell, z_s is the valency of the ion to which the standard electrode is reversible, a_s and a_{67} are the mean ionic activities of the salts in the two solutions, and $\Delta\psi$ is the so-called liquid junction potential calculated from the formula of Henderson [22]. It is best to eliminate $\Delta\psi$ by calculating its value and applying this as a correction straight away to the measured potentials ; this was done by Craxford [8]. It will be supposed that the $E_{Cal.}$ values have been corrected in this way. Then

$$dE_{Cal.} = dE_6 + \frac{RT}{z_6 F} dln a_{67}$$

$$= dE_6 - \frac{z_7}{-z_6 + z_7} dE_{67}$$

$$= \frac{-z_6 dE_6 + z_7 dE_7}{-z_6 + z_7}. \quad \text{. . . . (46)}$$

Equations (42) to (44) can now be recalculated, using the $E_{Cal.}$ reference-scale. Thus (43) becomes

$$\left(\frac{\partial E_{Cal.}}{\partial E_{67}}\right)_{Y,\,q_5,\,\gamma} = \frac{z_6 z_7 F}{-z_6 + z_7}\left(\frac{T_6 + T_7}{Q}\right);$$

$$\therefore \quad \left(\frac{\partial E_{Cal.}}{\partial \ln a_{67}}\right)_{Y,\,q_5,\,\gamma} = \frac{-RT}{F}\left(\frac{T_6 + T_7}{z_6 T_6 + z_7 T_7}\right), \quad . \quad (47)$$

and (44) becomes

$$\left(\frac{\partial E_{Cal.}}{\partial \ln a_{67}}\right)_{Y,\,q_5,\,Q} = -RT\left(\frac{\partial (T_6 + T_7)}{\partial Q}\right)_{Y,\,q_5,\,E_{67}}. \quad (48)$$

Now if $T_6 = 0$, the left-hand side of (47) becomes $\dfrac{RT}{z_7 F}$, and if $T_7 = 0$, it becomes $\dfrac{RT}{z_6 F}$. That is,

$$\left[dE_{Cal.} = -\frac{RT}{z_7 F}\,d\ln a_{67}\right]_{Y,\,q_5,\,\gamma,\,T_6=0}, \quad . \quad . \quad (49)$$

$$\left[dE_{Cal.} = -\frac{RT}{z_6 F}\,d\ln a_{67}\right]_{Y,\,q_5,\,\gamma,\,T_7=0}. \quad . \quad . \quad (50)$$

These shifts, which for a uni-univalent electrolyte become $\pm\dfrac{RT}{F}\,d\ln a_{67}$, will be called the standard shifts of the negative and positive branches respectively of the electrocapillary curve. Similarly, putting $d'T_6 = 0$ on the negative branch and $d'T_7 = 0$ on the positive branch, (44) gives

$$\left[dE_{Cal.} = -\frac{RT}{z_7 F}\,d\ln a_{67}\right]_{Y,\,q_5,\,Q,\,d'T_6=0}, \quad . \quad . \quad (51)$$

$$\left[dE_{Cal.} = -\frac{RT}{z_6 F}\,d\ln a_{67}\right]_{Y,\,q_5,\,Q,\,d'T_7=0}, \quad . \quad (52)$$

for the standard shifts of the two branches of the charge-potential curve.

Displacements of the magnitude of the standard shifts have several times been observed in practice. Philpot [9] has obtained experimentally shifts equal to those in equations (51) and (52) for the charge-potential curves of aqueous sodium and hydrogen chloride solutions. The corresponding standard shifts for electrocapillary curves

have been observed by Hansen and Williams [23] and by Craxford [8].

Philpot [9] has shown that Stern's theory of the double layer predicts shifts of the charge-potential curve equal to the standard ; but the fact that such shifts are observed in practice can hardly be regarded as supplying a stringent test of the theory. It is perhaps worth pointing out that it is impossible to obtain the standard shifts of the electrocapillary curve by integrating Stern's equation, because an unknown function of the concentration enters into the integration.

If the standard shift is observed for the electrocapillary curve, (49) and (50) show that T_6 and T_7 respectively vanish at potentials sufficiently far removed from the maximum on the negative and positive branches of the curve. If this is true of T_6 and T_7 it must be true of dT_6 and dT_7 also, so that the charge-potential curve too should undergo standard displacements. Now the vanishing of T_6 and T_7 respectively on the two branches corresponds roughly to saying that the double layer consists of anions only on the positive branch and cations only on the negative branch ; the correspondence is exact in sufficiently dilute solution. Hence the fact that standard shifts are observed in practice does not mean more than that the double layer is composed almost entirely of anions on the positive branch and of cations on the negative branch.

Deviations from the Standard Shift.

For a closer investigation of the displacements of the electrocapillary and charge-potential curves it is necessary to examine more precisely the meaning of the T's. Consider the volume element to which the n's in equations (4) and (5) refer. Let the volume of that part of it which lies on the solution side of the impenetrable boundary in the interphase be V, and let the density of the solution phase be D. Let

$$D_r = {}^2x_r D$$

for any constituent r of the solution only ; and define a quantity α_r for any constituent by means of the equation

$$n_r = VD_r + \alpha_r. \quad . \quad . \quad . \quad . \quad (53)$$

The physical significance of the α's is this. If the solution were homogeneous right up to the impermeable boundary at the interphase the α's would vanish; the α's are therefore measures of the surface excesses of the various constituents of the solution due to the inhomogeneity of the interphase, and are in fact Gibbs Γ's, expressed in moles cm.$^{-2}$, for a boundary coinciding with the actual impenetrable boundary instead of a more usual boundary of the type defined by putting some $\Gamma_r = 0$.

Inserting the values of the n's from equation (53) into (4) and (5) gives

$$T_6 = \alpha_6 - \frac{{}^2x_6}{{}^2x_{25}} \alpha_{25},$$

$$T_7 = \alpha_7 - \frac{{}^2x_7}{{}^2x_{25}} \alpha_{25},$$

$$Q = z_6\alpha_6 + z_7\alpha_7 - \frac{\alpha_{25}}{{}^2x_{25}} (z_6{}^2x_6 + z_7{}^2x_7)$$

$$= z_6\alpha_6 + z_7\alpha_7$$

(since the bulk part of phase 2 is electrically neutral). Hence the expression $\left(\dfrac{T_6 + T_7}{Q} \right)$ from equation (47) becomes

$$\frac{\alpha_6 + \alpha_7 - \dfrac{\alpha_{25}}{{}^2x_{25}} ({}^2x_6 + {}^2x_7)}{z_6\alpha_6 + z_7\alpha_7}. \quad \ldots \quad (54)$$

Suppose first that α_{25} is zero, so that (54) becomes simply $(\alpha_6 + \alpha_7)/(z_6\alpha_6 + z_7\alpha_7)$. This quantity takes on the standard values $\dfrac{1}{z_6}$ and $\dfrac{1}{z_7}$ respectively when α_7 and α_6 vanish. The vanishing of, say, α_7 means that the volume concentration of cations is the same right up to the interphase. In dilute solution this assumption tends asymptotically to the assumption that the solution side of the double layer consists of anions only, but in more concentrated solution the two hypotheses do not coincide. In fact we should expect cations to be positively adsorbed, attracted by the anion in the layer, so that α_7 would be somewhat positive; the shift in the electrocapillary curve should therefore be more than the standard shift.

At potentials on the positive branch further and further removed from the electrocapillary maximum α_6 becomes steadily larger. It might be thought therefore that at sufficiently positive potentials the large value of α_6 would outweigh any effect due to α_7 not quite vanishing, and that the shift would again reach the standard value. But this is not necessarily the case : as the layer builds up cations will be attracted more and more, so that α_7 will increase (numerically) as well as α_6. It is not unreasonable to suppose that the increases will be more or less proportional, in which case a constant shift larger than the standard shift will be observed on the branch in question.

A further complication arises when α_{25} does not vanish. In the first place the ions in the double layer must, in virtue of the volume they occupy, displace a certain number of solvent molecules from the layer next to the mercury. But this is unlikely to have an appreciable effect, because α_{25} is multiplied by the relatively small factor $\dfrac{{}^2x_6 + {}^2x_7}{{}^2x_{25}}$. Secondly, the solvent might be electrostricted in the double layer ; this would have an effect in the opposite direction to the one just mentioned. It would not be surprising to find quite considerable electrostriction with a solvent such as water ; water has a very open structure, and might easily pack more closely under the influence of the powerful forces at an interphase. The effect of electrostriction would be to give α_{25} an appreciable positive value. This would make the shift somewhat smaller than the standard shift. It may again be supposed that the effect increases roughly proportionally to the increase in α_6 on the positive branch (or α_7 on the negative branch), so that the effect does not disappear at potentials sufficiently far removed from the electrocapillary maximum. The effect will, however, disappear on diluting the solution, for the multiplying factor $\dfrac{{}^2x_6 + {}^2x_7}{{}^2x_{25}}$ is a measure of the concentration of the salt.

Specific Adsorption.

Reasons were found in the last section why the observed shift might sometimes differ slightly from the standard

shift. In practice it is frequently observed that the shift is larger, sometimes very much larger, than the standard shift. This phenomenon can be explained in terms of short-range forces of a specific chemical nature between the mercury and the anions of the solution; such a theory explains too certain related phenomena.

Fig. 5 (after Stern[17]).
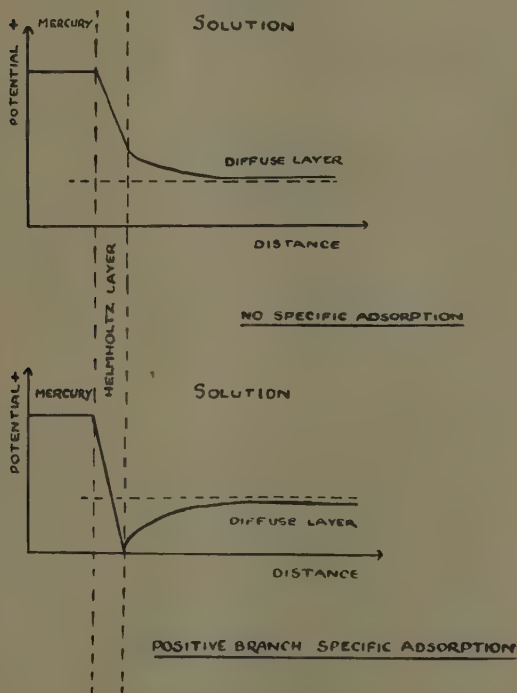
If an ion were strongly attracted by the mercury more of that ion would appear in the double layer than sufficed to balance the charge on the mercury side of the layer. This excess would be balanced by ions from the solution, of the opposite sign, in the diffuse part of the double layer. (The state of affairs is conveniently represented in a diagram showing the electrical potential plotted against distances from the interphase, as in fig. 5.)

Moreover, the excess of adsorbed ions and the balancing ions in the diffuse layer would together form what would be effectively a layer of ion-pair dipoles, which would give a boundary potential of their own reinforcing the applied external potential. This boundary potential might be further increased if actual adsorption of whole salt molecules from the solution, *e. g.*, by complex formation, occurred.

Ordinary inorganic cations are never specifically adsorbed in aqueous solution. It is possible that certain organic cations are, but the curves hitherto obtained are not accurate enough to distinguish between specific adsorption and a mere high capacity. Anions are usually specifically adsorbed in a range of 0·2 to 0·3 volt on the negative side of the potential of the $Hg : Hg_2X_2$ electrode, X being the anion in question. There is thus considerable specific attraction between the mercury and the ion before a potential sufficiently positive for discharge is reached ; this suggests that a dropping mercury electrode might find application in the concentration of small quantities of physiologically interesting substances from solutions.

The phenomena observed when specific adsorption occurs are these :—

(*a*) The concentration shifts of the electrocapillary and charge-potential curves are no longer equal to the standard shifts, but are very much larger. The reason for this is that $z_6F\mathcal{T}_6$ can no longer be identified even approximately with $-Q$ on the positive branch. In fact $z_6F\mathcal{T}_6 >> Q$ (numerically) and $z_6Fd\mathcal{T}_6 >> dQ$ (numerically) ; so it follows from equations (47) and (48) that the shifts of both curves are larger than in the absence of specific adsorption. Craxford [8] has obtained electrocapillary curves for potassium iodide which show this phenomenon quite clearly : the shifts are normal on the negative branch and very much larger on the positive branch. Further, on differentiating these curves, charge-potential curves are obtained which have no linear part at all on the positive side and again show an abnormally large dilution shift.

(*b*) The charge-potential curve rises steeply until it is very nearly vertical at the potential of the $Hg : Hg_2X_2$ electrode : Koenig's curve for potassium nitrate [15] shows this quite clearly. This is evidently due to the

reinforcement of the externally-applied potential by the boundary potential due to the adsorption as discussed already ; this reinforcement increases the capacity of the double layer. If the salt Hg_2X_2 is very insoluble the interphase remains completely polarizable almost up to the potential of the $Hg : Hg_2X_2$ electrode, so that an identification of the slope of the electrocapillary curve with the charge on the double layer is possible throughout. If the salt Hg_2X_2 is more soluble, mercury ions begin to be electrolyzed into the solution before the $Hg : Hg_2X_2$ potential is reached, so the above identification is no longer possible. But this can hardly affect the main conclusion.

(c) A third phenomenon which usually accompanies specific adsorption is a shift in the potential of the electrocapillary maximum and a lowering of the surface tension there. At the maximum $-Q = z_6 F T_6 + z_7 F T_7 = 0$ as usual, but T_6 and T_7 are not small. Consequently the ions again form what is effectively a layer of ion-pair dipoles on the solution side of the interphase, with a boundary potential of its own. The ion-pair layer probably modifies, too, that part of the boundary potential due to the solvent dipoles : the net variation in the boundary potential appears as the shift of the electrocapillary maximum. This effect on the boundary potential must increase progressively as the potential is made more positive, and is, as has been shown, the cause of the high capacities observed when specific adsorption occurs.

The decrease in the surface tension at the maximum follows from equation (45). In the absence of specific adsorption T_7 is very small at the maximum and the surface tension is very nearly that of pure water. For specifically adsorbed substances the appreciable size of T_7 results in a fairly considerable lowering of the surface tension relative to pure water, and hence relative to salts which are not specifically adsorbed.

The Effect of added Non-Electrolytes on Electrocapillary Curves.

Nearly all non-electrolytes can be considered as yielding a common ion with the solvent, so that the system is again a special case of system 1, in which only electrode 3 is omitted. If the added substance, *e. g.*, carbon tetra-

bromide, is incapable of yielding one of the ions of the solvent an extra electrode must be introduced into the system ; but provided the added substance is unionized and does not react chemically with the solvent the treatment of the two cases does not differ in essential particulars. Attention will therefore be confined to systems which are of the type of system 1, with electrode 3 omitted.

The most convenient network of circuits is $1—R$, $5—R$, $6—R$, $7—R$, $2—5$, $4—5$. Surface adsorptions are again calculated to the basis $T_1 = T_{25} = 0$, so circuits $1—R$ and $2—5$ are unnecessary. The reasons for putting subscript q_5 in place of E_5 are presumably still valid provided the added substance is unionized, so circuit $5—R$ can also be omitted. Equations (29)–(32), (35)–(40), and (42)–(45) are then still valid with the additional suffix E_{45}.

It is, too, often possible to put q_{45} in place of E_{45} in the list of suffixes. For instance, for equation (37) the necessary condition is that the difference term

$$\left[\left(\frac{\partial \gamma}{\partial E_{45}} \right)_{E^*} \left(\frac{\partial E_{45}}{\partial E_6} \right)_{q_{45}} \right]_{Y,\, q_5,\, E_{67}} \quad . \quad . \quad (55)$$

should be small in comparison with the $z_r F T_r$ terms. This is true for all but very strongly positively adsorbed non-electrolytes ; for $\left(\dfrac{\partial \gamma}{\partial E_{45}} \right)_{Y,\, q_5,\, E^*,\, E_{67}}$ is of the order of magnitude of the $z_r F T_r$ terms, and $\left(\dfrac{\partial E_{45}}{\partial E_6} \right)_{Y,\, q_5,\, q_{45},\, E_{67}}$ is numerically small because E_{45}, but not E_6, cannot be appreciably altered under the conditions of constancy imposed. Such a substitution is possible in equations (29), (32), and (40), in addition to (37).

A third approximation can now be applied to equation (37), namely, the replacement of E_{67} by q_7, for essentially the same reason as in the absence of an added non-electrolyte. Thus the final equation is

$$\left(\frac{\partial \gamma}{\partial E_6} \right)_{Y,\, q_5,\, q_{45},\, q_7} = -Q. \quad . \quad . \quad . \quad (56)$$

Equation (32) could be treated similarly. Equation (56) is of considerable importance, because it shows that even when the electrocapillary curve is considerably distorted it is still possible to obtain the charge on the double layer by differentiation. Frumkin[10] has obtained

experimental confirmation of this result by comparing dropping electrode and electrocapillary data.

The use of the condition $dq_{45}=0$ in place of $dE_{45}=0$ is not in general possible for a very strongly adsorbed non-electrolyte, *e. g.*, for a grease, because neither of the differential coefficients in expression (55) is necessarily small enough. The $\left(\dfrac{\partial \gamma}{\partial E_{45}}\right)$ term in particular is known to be large.

The substitution in question is moreover invalid in equations (41) to (45) for all non-electrolytes, so that investigations of dilution shifts in presence of additional non-electrolytes would have to be made keeping the chemical potential of the non-electrolyte constant (*i. e.*, keeping E_{45} constant). The reason for this is that the difference term in each case contains a differential co-efficient $\left(\dfrac{\partial E_{45}}{\partial E_{67}}\right)$ which is not necessarily small.

A similar difficulty arises in attempting to find T_{45} from the equation

$$\left(\frac{\partial \gamma}{\partial E_{45}}\right)_{Y,\,E_5,\,E_6,\,E_{67}} = z_{45}FT_{45}, \quad . \quad . \quad . \quad (57)$$

which follows directly from the general electrocapillary equation (3). As usual, q_5 can be put for E_5, but the replacement of E_{67} by q_7 could be made only if $\left(\dfrac{\partial E_{67}}{\partial E_{45}}\right)_{Y,\,q_5\,q_7,\,E_6}$ were numerically small ; this is not in general the case. The correct way to apply (57) would therefore be to observe the lowering of surface tension on adding a non-electrolyte to a solution in which the salt is kept at constant chemical potential (*i. e.*, at constant E_{67}).

Expressed in general terms the difficulty which arises is that the salt and the non-electrolyte influence each other's chemical potentials (or activities). If this inter-action can be neglected the desired substitutions of exten-sive for intensive restrictions are valid : this is often the case when one of the substances is at a low concentration compared with the other.

An additional difficulty arises over the potential scale. Equation (57) and the equations for dilution shifts necessi-tate the use of an E_6-scale, whereas measurements are usually made on an $E_{Cal.}$-scale. There has been developed

for this case no theory like the theory of liquid junction potentials between electrolytic solutions in the same solvent, so that a correlation of the two scales is not possible. This difficulty has hitherto been overlooked.

The best way therefore to discuss the effect of non-electrolytes is to consider their effect on the capacity of the double layer rather than to attempt to calculate the surface adsorption of the non-electrolyte. In general a non-electrolyte lowers the electrocapillary curve around the maximum, but leaves it more or less unchanged at potentials well removed from the maximum. The latter part of the effect is easily explained : at potentials away from the maximum the large charge on the double layer causes the more polar water to displace the less polar non-electrolyte from the interphase, owing to a salting-out effect. This restores the interphase to the state it would assume in the absence of the non-electrolyte ; so the surface tension returns to its ordinary value. This theory accords with the fact that with strongly polar substances, such as urea (which is probably a zwitter-ion), the curve is lowered considerably even at potentials far away from the maximum (Gouy [24]).

In accounting for the effect of a non-electrolyte on the region around the maximum it must not in general be supposed that the mercury plays any essential part in the phenomenon. The evidence for this comes from a comparison of the behaviour of non-electrolytes at the solution-mercury interphase with their behaviour at the solution-air interphase. Frumkin [25] has shown in a large number of cases that the change in the solution-air boundary potential on the addition of a non-electrolyte to an aqueous solution is nearly the same as the corresponding shift in the potential of the electrocapillary maximum for the solution-mercury interphase. The only important exceptions to this rule are sulphur-containing compounds, which do appear to be specifically attracted to the mercury.

The low capacities around the maximum when a non-electrolyte is added might be attributed to the separation of the charges on the two sides of the double layer by an adsorbed film of non-electrolyte. This is probably what occurs when the surface is contaminated by grease, but seems an unlikely explanation when the adsorbed film is known to be far from continuous. Another

argument against this as a general theory is that, though addition of alcohol to aqueous solutions causes a flattening of the maximum, the flattened portions are not observed in pure aqueous or pure alcoholic solutions : it can hardly be supposed that the ions penetrate to the mercury in the two pure solvents but not in mixtures of them.

Instead it seems reasonable to suppose that the molecules of the non-electrolyte are present along with solvent molecules and ions in the layer next to the mercury. Then it may be supposed that the lines of electrostatic force from the mercury spread out through the molecules of the solvent and of the non-electrolyte, and that this spreading and the fall of potential will depend on the composition of the layer next to the mercury : such a theory has already been advanced to account for the effect of the solvent on the capacity of cations. On this theory very low capacities are due in the main to a secondary effect, just as the high capacities of specifically adsorbed ions are due to a secondary effect. The effect in question is this : small changes in surface charge cause a considerable alteration in the ratio of solvent molecules to molecules of added non-electrolyte in the double layer. This salting-out effect involves a redistribution of oriented dipoles at the interphase, and consequently a considerable change in the interfacial potential.

In general then near the maximum the non-electrolyte is salted out of the solution on to the interphase, and away from the maximum the accumulation of electric charge salts it back into solution.

No instance of negative adsorption of a non-electrolyte added to an aqueous solution is known, but water added to alcoholic LiCl raises the surface tension in the region of the maximum (Frumkin [26]), and must therefore be negatively adsorbed. The water increases the capacity of the double layer instead of decreasing it.

This result is in agreement with the theory given above, since water has a higher dielectric constant than alcohol.

Amalgams.

System 1 is appropriate for dealing with amalgams. The surface adsorption of thallium is given by the equation

$$\left(\frac{\partial \gamma}{\partial E_3} \right)_{\gamma,\, E_{45},\, E_5,\, E_6,\, E_{67}} = z_3 F \Gamma_3, \quad . \quad . \quad (58)$$

where E_5 can be replaced by q_5, E_{45} by q_{45}, and E_{67} by q, as before. Moreover, equations (28)–(52), (56), and (57) are still valid with the added suffix E_3. This suffix can be replaced by the suffix q_3 unless the thallium is very strongly adsorbed ; hence

$$\left(\frac{\partial \gamma}{\partial E^*}\right)_{Y, q_3, q_{45}, q_5, q_7} = -Q, \quad . \quad . \quad . \quad (59)$$

so that the charge on the double layer can again be found by differentiation of ordinary electrocapillary data.

The variation of the electrocapillary maximum is of special interest. Thus the identity

$$\left[\left(\frac{\partial \gamma}{\partial E_3}\right)_{Q=0} = \left(\frac{\partial \gamma}{\partial E_3}\right)_{E_6} + \left(\frac{\partial \gamma}{\partial E_6}\right)_{E_3}\left(\frac{\partial E_6}{\partial E_3}\right)_{Q=0}\right]_{Y, q_{45}, q_5, q_7}$$

reduces to

$$\left[\left(\frac{\partial \gamma}{\partial E_3}\right)_{Q=0} = \left(\frac{\partial \gamma}{\partial E_3}\right)_{E_6}\right]_{Y, q_{45}, q_5, q_7}$$

$$= z_3 F \mathcal{I}_3 \quad . \quad . \quad . \quad . \quad . \quad (60)$$

at the maximum, since $\left(\dfrac{\partial E_6}{\partial E_3}\right)_{Y, q_{45}, q_5, q_7, Q=0}$ does not in general become indefinitely large.

Now the effect of amalgamation is essentially simply to displace the whole curve bodily along the potential axis. Consequently the left-hand side of (60), and hence the surface adsorption of thallium at the maximum, vanishes. The horizontal displacement of the curve is given by

$$\left[\left(\frac{\partial E_6}{\partial E_3}\right)_{\gamma} = -\left(\frac{\partial \gamma}{\partial E_3}\right)_{E_6}\bigg/\left(\frac{\partial \gamma}{\partial E_6}\right)_{E_3}\right]_{Y, q_{45}, q_5, q_7}$$

$$= -\frac{z_3 F \mathcal{I}_3}{Q}, \quad . \quad . \quad . \quad . \quad . \quad (61)$$

which reduces to $0/0$ at the maximum. Hence arises the interesting fact that a horizontal displacement of the curve implies surface adsorption of thallium everywhere but at the maximum. The experimental fact that the horizontal displacement is more or less constant over the curve means that $\mathcal{I}_3$ must be approximately proportional to Q.

Since the horizontal shift of the maximum is not directly caused by adsorption an alternative explanation must be found. The natural explanation would seem to be that the different electron affinities of the metallic constituents of phase 1 are responsible. Consider, for example, the circuit shown in fig. 6.

The five $\Delta\phi$ terms refer to Galvani potential differences (see Lange and Miscenko [26]). At constant pressure, temperature, and composition of the solution $\Delta\phi_3$, $\Delta\phi_4$, and $\Delta\phi_5$ can be supposed to be fixed even if the composition of the amalgam changes. Thus alteration in the composition of the amalgam can affect only $\Delta\phi_1$ and $\Delta\phi_2$. If the amalgam is kept at the electrocapillary maximum it may be further supposed that $\Delta\phi_2$ does not alter greatly : there is good reason for thinking this, because

Fig. 6.
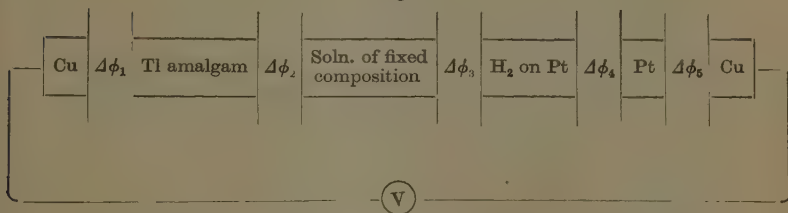
the solution side of the interphase is unchanged throughout and no surface adsorption occurs on the metallic side. The shift in the maximum may then be ascribed to $\Delta\phi_1$, and so to the differing Galvani potentials of the metals involved. This is in marked contrast to the reversible hydrogen electrode potential, which is the same for all metals irrespective of their Galvani potentials. This latter result follows directly from the law of excluded perpetual motion (Butler [28]) and is a well-known experimental fact.

Capillary Adsorption.

Explanations of two experimental results are given in this section : (1) the addition of a small quantity of another substance may lower the surface tension of a liquid considerably, but has never been observed to raise it to more than a slight extent; and (2) Gibbs's adsorption equation gives results in direct agreement with Langmuir-

Adam trough experiments when applied to films of lauric acid on water.

Applying equations (4) and (5) to system 4,

$$n_1 = \lambda_1 \,^1x_1 + \lambda_2 \,^2x_1,$$
$$n_2 = \lambda_1 \,^1x_2 + \lambda_2 \,^2x_2,$$
$$n_3 = \lambda_1 \,^1x_3 + \lambda_2 \,^2x_3 + T_3.$$

Hence, eliminating λ_1 and λ_2, and using (24),

$$\begin{vmatrix} ^1x_1 & ^2x_1 & n_1 \\ ^1x_2 & ^2x_2 & n_2 \\ ^1x_3 & ^2x_3 & n_3 + \left(\dfrac{\partial\gamma}{\partial\bar{\mathrm{F}}_3}\right)_{\mathrm{Y}} \end{vmatrix} = 0, \quad . \quad . \quad (62)$$

where Y implies constancy of s, X′, N_1, and N_2.

If 2 and 3 are absent from phase 2, (62) reduces to

$$\begin{vmatrix} ^1x_2 & n_2 \\ ^1x_3 & n_3 + \left(\dfrac{\partial\gamma}{\partial\bar{\mathrm{F}}_3}\right)_{\mathrm{Y}} \end{vmatrix} = 0,$$

provided $^2x_1 \neq 0$ (*i. e.*, provided phase 2 exists). Therefore

$$\frac{\partial\gamma}{\partial\bar{\mathrm{F}}_3} = \frac{^1x_3}{^1x_2} n_2 - n_3 = -T_3. \quad . \quad . \quad (63)$$

If phase 2 does not exist (63) still holds for a two-component system, for in such a case only one T can be made to vanish and there are only two equations :

$$n_2 = \lambda x_2,$$
$$n_3 = \lambda x_3 + T_3.$$

The following theory applies equally well to both cases.

If no adsorption occurs $\dfrac{n_2}{n_3} = \dfrac{^1x_2}{^1x_3}$, and γ is unaltered by the addition of 3. If 3 is positively adsorbed $\dfrac{n_2}{n_3} < \dfrac{^1x_2}{^1x_3}$, and γ is lowered. If 3 is negatively adsorbed $\dfrac{n_2}{n_3} > \dfrac{^1x_2}{^1x_3}$, and γ is raised. Writing N for $n_2 + n_3$ in (63) yields

$$T_3 = n_3\left(1 + \frac{^1x_3}{^1x_2}\right) - \frac{^1x_3}{^1x_2}N$$

$$= N - n_2\left(1 + \frac{^1x_3}{^1x_2}\right). \quad . \quad . \quad . \quad . \quad (64)$$

Now T_3 is independent of λ_1 and λ_2, *i. e.*, of N. There is, however, a minimum possible value of N, say $N_{min.}$, because the element of volume to which N and the n's refer must contain the whole of the inhomogeneous region between the two phases and also traces of both homogeneous bulk phases. The value of $N_{min.}$ depends on the extent of the inhomogeneous region in the given system. There is good reason to believe that for almost all neutral molecules $N_{min.}$ lies between fairly narrow limits corresponding to an inhomogeneous region not much thicker than a unimolecular layer. Now $\dfrac{dT_3}{dN}$ must vanish when $N \geqq N_{min.}$ if T_3 is to have a physical meaning as defined in the introduction ; so that all the information in (64) is given equally well with $N_{min.}$ in place of N. Since all the n's and x's are positive, it follows that

$$-\frac{^1x_3}{^1x_2} \cdot N_{min.} \leqq T_3 \leqq N_{min.} \quad . \quad . \quad . \quad (65)$$

If therefore $^1x_3 << {}^1x_2$ (*i. e.*, for small additions of 3), the limit of negative adsorption is small in general compared with the limit of positive adsorption. Moreover $N_{min.}$ is much more likely to be abnormally large for positive than for negative adsorption ; so a considerable lowering of the surface tension by a trace-component is much more likely than a large rise.

If component 3 is confined to the interphase, so that $^1x_3$ and $^2x_3$ are zero, it follows at once that

$$-\left(\frac{\partial\gamma}{\partial F_3}\right)_T = T_3 = n_3. \quad . \quad . \quad . \quad (66)$$

Hence $-\left(\dfrac{\partial\gamma}{\partial F_3}\right)_T$ gives directly the surface concentration in moles/cm.^{2}. This is why the application of the Gibbs adsorption equation to a film of lauric acid on water

gives results in direct agreement with Langmuir-Adam trough experiments.

The authors would like to thank B. Higman for his helpful suggestions during the preparation of this paper.

Summary.

1. The electrocapillary equation obtained in papers I., II., and III. of this series is explained and applied to three typical electrocapillary systems ; a fourth system containing no ionizing components is also discussed.

2. The special properties of a completely polarizable interphase are discussed and reasons are given for believing that the solution-mercury interphase is usually completely polarizable.

3. Ordinary electrocapillary curves of salt solutions are considered. Certain necessary approximations for interpreting existing data are shown to be valid. The structure of the double layer and the capacities of ions in the layer are dealt with. The dilution shifts of electrocapillary and charge-potential curves are shown to be capable of yielding considerable information about the structure of the double layer ; the question of the potential scale is treated incidentally here. Finally, an attempt is made to give a more precise meaning to the term " specific adsorption " ; it is shown that several related phenomena can be explained by means of a single simple hypothesis.

4. The effect of non-electrolytes on the electrocapillary curve is dealt with. Certain difficulties of interpretation, not hitherto appreciated, are pointed out, and it is shown that a consideration of the capacity of the double layer affords the best basis for discussion.

5. Electrocapillary curves of amalgams are discussed, and attention is drawn to a feature hitherto overlooked. It is suggested that the different Galvani potentials of different metals are largely responsible for the displacement of the curve on amalgamation.

6. Two problems in capillary adsorption are treated.

Note added in proof.—It should perhaps be made clear that an equation of the Lippmann form, exact apart from the volume-correction term, must always hold provided that there is only one external circuit. In such a case, $C-1$ of the dq's must be put equal to zero,

and it follows from the general electrocapillary equation (1) that (neglecting the volume-correction term)

$$\left[\left(\frac{\partial \gamma}{\partial E_{rs}} \right)_s = \left(\frac{\partial q_{rs}}{\partial s} \right)_{E_{rs}} \right]_{X, (C-1)q'_s}, \quad \cdot \quad \cdot \quad (67)$$

where the one remaining circuit is the one connecting electrodes r and s, one of which may be the reference electrode.

If the interphase is completely polarizable, equation (67) must be interpreted in two different ways according as the ions to which electrodes r and s are reversible are both in the same phase or not. If the ions are in different phases, then (67) is simply the Lippmann-Helmholtz equation in Lippmann's original form. dq_{rs} is an element of charge flowing from one phase to the other, so that the slope of the electrocapillary curve is precisely equal to the rate of increment of the charge on the double layer as the interphase is expanded at constant E_{rs}.

Equations (41), (56), and (59) are nevertheless of more importance than (67), because the left-hand side of the latter cannot be identified, except approximately, as the charge per unit area of the interphase; it is only when all intensive variables are constant that such an identification can be made. Moreover, equation (67) yields no information about the relationship of the slope of the electrocapillary curve to the T's. It must, however, be pointed out that the agreement of the various measurements of the capacity of the double layer (8), (9), (10), (13) really affords a test of equation (67) rather than of our approximate equation (41).

If electrodes r and s are in the same phase, equation (67) is an exact equation giving (for different choices of r and s) the effects of diluting the solution, adding a non-electrolyte, and adding a second metal to the mercury phase. But it does not displace such equations as (42) and (60), because, as before, the $\dfrac{\partial q_{rs}}{\partial s}$ term in it cannot be related to the T's (and hence to the structure of the interphase) except by means of the approximations already discussed.

It should also be remarked that many of the correction terms discussed, and for the most part shown to be negligible, can be made indefinitely small by increasing the size of one or both bulk phases. In fact the only

exceptions are the correction terms neglected in the deduction of the equations for dilution shifts in presence of a non-electrolyte, and of equation (57); it has, however, already been shown that the substitutions of q_{45} for E_{45} (in the dilution shift equations) and of q_7 for E_{67} (in equation (57)) are invalid.

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XXX. *The Theory of Electrocapillarity.*—V. *A Note on the Definition of Surface Tension. By* O. GATTY *and* H. A. C. McKAY *.

IN papers I. to III. of this series [1] a thermodynamic theory of electrocapillarity has been developed so as to be adequate for the applications treated in paper IV.,

which shows how surface adsorptions and the capacity of the double layer are related to existing electrocapillary data. The capacity of the double layer and the question of specific adsorption are still found to be the outstanding problems of electrocapillarity ; they should be easier to investigate with the more precise theoretical technique developed in these papers.

The theory was developed by considering how surface work is actually performed in an idealized apparatus that includes the essential features of any apparatus for measuring surface tension ; previous treatments had tended rather to introduce the surface tension as a physical concept with certain properties rather arbitrarily ascribed to it. It was shown in paper I. that the consideration of the work done on the idealized apparatus leads to a definition of surface tension in agreement with that of Laplace and Young. The theory showed unequivocally for the first time that surface work, defined in terms of the classical surface tension, does *not* include compressional work due to volume changes on emulsification. The treatment given in paper I. is, however, incomplete ; the purpose of the present note is to clarify and extend that treatment.

In the first place, it can be shown that the possible compressibility of the containing-vessel does not affect the theory. The procedure in proving this is straightforward though lengthy, and need not be given here. It emerges that the total mechanical work done during an infinitesimal displacement of the pistons is given by the sum of a series of compressional terms *plus* a term containing the factor $(p_1 - p_2)$, which may be taken as the surface work term *. If the containing vessel is incompressible the only compressional terms remaining are

$$-p_1 \, dV_1 - p_2 \, dV_2$$

(the terms for the two bulk phases), while the surface work term becomes

$$(p_1 - p_2)_2 \, dv_{12}.$$

Equations (6) and (7) of paper I. refer to a hypothetical expansion at constant area for all surfaces in the system except the 12 interphase. For actual surface expansions, which generally involve more interphases than one, they

* Paper I., p. 858, the expression at the bottom should read
$$\delta W = -p_2 dV.$$

must be replaced in the case of an incompressible containing-vessel by

$$\delta W = -p_1 \, dV_1 - p_2 \, dV_2 + (p_1 - p_2) \, dv_{12}$$

and

$$\delta W = -p_1 \, dV_1 - p_2 \, dV_2 + \Sigma \gamma \, ds$$

respectively, where $(p_1 - p_2) \, dv_{12}$ is set equal to $\Sigma \gamma \, ds$ after the manner of (3) of paper I., but using γ instead of γ' terms and defining the s_Δ's, as is physically possible, so that $ds_{ij\Delta} << ds_{ij}$. It is supposed that there is no gravitational field.

In this equation v_{12} is the volume swept out by any arbitrary surface whatsoever between phases 1 and 2, varying in any arbitrary manner whatsoever during a movement of the pistons. But it is only for a certain type of surface that the surface work can be expressed in the form $\Sigma \gamma \, ds$, where the s's are the areas of all the interphases in the system and the γ's are not functions of position in these interphases.

There are three interphases to consider, namely, 12, 13, and 23 (phase 3 is the containing-vessel itself). Hence $\Sigma \gamma \, ds$ is equal to

$$\gamma_{12} \, ds_{12} + \gamma_{13} \, ds_{13} + \gamma_{23} \, ds_{23}.$$

Part of the change in s_{13} occurs in the neighbourhood of piston 1 and part of that in s_{23} in the neighbourhood of piston 2. These parts can, however, be made as small as desired by increasing the cross-sections of the pistons ; so ds_{13} and ds_{23} can be taken to refer to the changes in s_{13} and s_{23} in the neighbourhood of the 12 interphase only. It follows that $ds_{13} + ds_{23} = 0$, since the containing-vessel is assumed incompressible (the result is also valid under suitable conditions in the general case), so that $\Sigma \gamma \, ds$ becomes

$$\gamma_{12} \, ds_{12} + (\gamma_{13} - \gamma_{23}) \, ds_{13}.$$

It will be assumed, then, that there exists a type of surface such that

$$(p_1 - p_2) \, dv_{12} = \gamma_{12} \, ds_{12} + (\gamma_{13} - \gamma_{23}) \, ds_{13}, \quad . \quad (1)$$

where s_{12} refers to the same surface as v_{12} and the γ's are constant over their respective interphases. It will be shown that such a surface must have the same curvature at all points and must make the same angle of contact at every point where it meets the wall of the containing

vessel. Conversely it will be shown that these are sufficient conditions to ensure the validity of (1).

First, put $ds_{13}=0$, so that (1) becomes

$$[(p_1-p_2)\,dv_{12}=\gamma_{12}\,ds_{12}]_{s_{13}}. \quad . \quad . \quad . \quad (2)$$

Suppose that a small rectangular element is described in the following way in the surface to which v_{12} and s_{12} refer. Any pair of points sufficiently close together in the surface are taken, and the planes containing the principal circles of curvature are constructed at each of these points. The intersections of these four planes with the surface delimit an element of area δs_{12} (say) on the surface. The whole surface may be split up into elements in this way. Further, the region bounded by the four planes, the surface, and any arbitrary fixed surface intersecting the four planes may be taken as an element of volume, δv_{12}.

During a displacement of the pistons every point on such an element of the surface will be displaced an infinitesimal amount, say ϵ; since the element is vanishingly small, ϵ may be taken as constant. If the displaced surface is divided into elements by the identical network of planes which divided the undisplaced surface, then the change in δv_{12} must be given by

$$d(\delta v_{12})=\epsilon\,\delta s_{12}$$

(d is used, as in equation (1), to designate infinitesimals referring to the process of displacement; d and δ, of course, commute so that $d(\delta v_{12})=\delta(dv_{12})$ etc.). Moreover, it is a well-known result that

$$d\,\delta s_{12}=\epsilon\mathrm{K}\,ds_{12}=\mathrm{K}d\,\delta v_{12}, \quad . \quad . \quad . \quad (3)$$

where K is the mean curvature; K is equal to $\dfrac{1}{\mathrm{R}_1}+\dfrac{1}{\mathrm{R}_2}$, where R_1 and R_2 are the principal radii of curvature of the surface.

By differentiation of (2)

$$[(p_1-p_2)\delta\,dv_{12}=\delta\gamma_{12}\,ds_{12}+\gamma_{12}\delta\,ds_{12}$$
$$=\delta\gamma_{12}\,ds_{12}+\mathrm{K}\gamma_{12}\delta\,dv_{12}]_{s_{13}}.$$

Now γ_{12} does not vary over the surface, so $\delta\gamma_{12}=0$. Hence

$$\gamma_{12}=\frac{p_1-p_2}{\mathrm{K}}. \quad . \quad . \quad . \quad . \quad (4)$$

Hence also K is constant over the surface.

Constancy of the angle of contact, β, is proved by making use of the constancy of $(\gamma_{13}-\gamma_{23})$ round the boundary of the surface, *i. e.*, the region where it intersects (or touches) the containing vessel. Let a normal to the undisplaced surface traverse this boundary ; this normal will delimit a certain region in the displaced surface (produced, if necessary, into phase 3). Let $d'v_{12}$ and $d's_{12}$ be the changes in v_{12} and s_{12} respectively on passing from the undisplaced surface to this limited region in the displaced surface. Then, by integrating (3) over the whole surface, it follows that

$$d's_{12}=\text{K}d'v_{12}, \quad . \quad . \quad . \quad . \quad (5)$$

for K is constant over the surface. $d'v_{12}$ and $d's_{12}$ differ from dv_{12} and ds_{12} respectively by the small annular regions round the boundary. These regions can be split into elements by a series of planes perpendicular to the surface described by the normal to the boundary of the undisplaced surface.

Each small element of volume described in this way can be treated as a rectangular triangular prism. Let δ' refer to any of the properties of such an element, so that $\delta'(dv_{12}-d'v_{12})$, for instance, is its volume. The element is vanishingly small, so that β, the angle of contact, can be taken as constant over the element ; hence

$$\delta'(ds_{12}-d's_{12})=-\cos\beta\delta'ds_{13}. \quad . \quad . \quad (6)$$

The negative sign is introduced to make $\beta\leq 90°$ when the concave side of the 12 surface faces phase 1.

By combination of (1) and (4)

$$\gamma_{12}(\text{K }dv_{12}-ds_{12})=(\gamma_{13}-\gamma_{23})\,ds_{13}.$$

Hence from (5)

$$\gamma_{12}[\text{K}(dv_{12}-d'v_{12})-(ds_{12}-d's_{12})]=(\gamma_{13}-\gamma_{23})\,ds_{13}.$$

This is now in a form to be differentiated round the periphery of the 12 surface. It is found that

$$\gamma_{12}[\text{K}\delta'(dv_{12}-d'v_{12})-\delta'(ds_{12}-d's_{12})]$$
$$=\delta'(\gamma_{13}-\gamma_{23})\,ds_{13}+(\gamma_{13}-\gamma_{23})\delta'ds_{13}. \quad . \quad . \quad (7)$$

Now $\text{K}\delta'(dv_{12}-d'v_{12})$ is equal to $\text{K}\epsilon\delta'(ds_{12}-d's_{12})$, where ϵ is the normal displacement of a point on the boundary of the original 12 surface. Since the displacement dealt with is a vanishingly small one ($\epsilon\rightarrow 0$) this term can be

neglected in comparison with $\delta'(ds_{12}-d's_{12})$. Hence by putting $\delta'(\gamma_{13}-\gamma_{23})$ equal to zero, it follows from (6) and (7) that

$$\gamma_{13}-\gamma_{23} \quad \gamma_{12}\cos\beta, \quad \ldots \quad (8)$$

and from this that β is constant round the boundary.

It has now been shown that constancy of K and β are necessary properties of a surface for which (1) holds. They are also sufficient properties to ensure the validity of this equation. For consider any surface having these properties. (6) is, of course, still valid, and can be inte· grated round the boundary to give

$$ds_{12}-d's_{12}=-\cos\beta\,ds_{13},$$

for $\cos\beta$ is constant. Since K is constant over the surface, (5) still holds, so that

$$ds_{12}-Kd'v_{12}=-\cos\beta\,ds_{13}.$$

For reasons similar to those mentioned after equation (7) $d'v_{12}$ can be replaced by dv_{12}, so that finally

$$Kdv_{12}=ds_{12}+\cos\beta\,ds_{13},$$

which is an equation of the form of (1). Equations (4) and (8) follow by equating coefficients.

Actual measurable " physical " surfaces (such as the optical surface) are almost certainly of the type so far considered, provided the total surface area is small enough for the effects of gravity to be neglected. In the first place there is the experimental fact that any such surface tends to minimum area (or maximum area in the case of complete miscibility), a property which is expressed by the equation

$$[ds_{12}=0]_{v_{12},\,s_{13}} \quad \ldots \quad \ldots \quad (9)$$

Moreover the 13 and 23 surfaces are also physical surfaces. The total area of these surfaces is constant, so that the one containing the smaller surface energy per unit area will tend to grow at the expense of the other. That is

$$[ds_{13}=0]_{v_{12},\,s_{12}}. \quad \ldots \quad \ldots \quad (10)$$

(9) and (10) together imply the existence of an equation of the form of (1). In the second place it is an experimental fact that $\dfrac{p_1-p_2}{K}$ and β are constant for the optical surface. The observed constancy of γ_{12} over the optical surface is in agreement with the concepts that

it is a physical property of this surface and that it measures the energy due to the two different energies of interaction of the bulk phases with the interphase (see paper I., p. 851). Interactions of the type mentioned cannot be readily defined except in terms of the energy used in some thermodynamic process. They would not, however, be expected to vary with radii of curvature unless the latter were of a size comparable to the thickness of the non-homogeneous region separating phases 1 and 2. Thus any measure of such interactions should remain constant over all ordinary interphases, which is just what is found for γ_{12}.

For the special case of a conical capillary the problem can be treated by more elementary methods. It can be assumed that the surface is symmetrical about the axis of the capillary and that the boundary of the surface is circular, and so from (9) the surface must be spherical.

Let the cone of the capillary have a half-angle α, let β be the angle of contact as before, and let l be the distance of a point on the boundary of the 12 surface from the apex of the cone. It can be shown by trigonometry that

$$v_{12} = \text{constant} + \frac{\pi l^3}{3}\left(\frac{\sin^2 \alpha}{\cos^3 \overline{\alpha+\beta}}\right)(2\sin\alpha - 2\sin\alpha \, . \, \sin\overline{\alpha+\beta} - \cos\beta \, . \, \cos^2\overline{\alpha+\beta}),$$

$$s_{12} = 2\pi l^2\left(\frac{\sin^2\alpha}{\cos^2\overline{\alpha+\beta}}\right)(1 - \sin\overline{\alpha+\beta}),$$

$$s_{13} = \text{constant} - \pi l^2 \sin\alpha.$$

Hence, when α (but not β) is invariable,

$$dv_{12} = -\pi l^2\left(\frac{\sin^2\alpha}{\cos^3\overline{\alpha+\beta}}\right)(2\sin\alpha - 2\sin\alpha \, . \, \sin\alpha+\beta$$

$$- \cos\beta \, . \, \cos^2\overline{\alpha+\beta})dl - \pi l^3\left(\frac{\sin^3\alpha}{\cos^4\overline{\alpha+\beta}}\right)(1 - \sin\overline{\alpha+\beta})^2 d\beta,$$

$$ds_{12} = 4\pi l\left(\frac{\sin^2\alpha}{\cos^2\overline{\alpha+\beta}}\right)(1 - \sin\overline{\alpha+\beta}) \, dl$$

$$- 2\pi l^2\left(\frac{\sin^2\alpha}{\cos^3\overline{\alpha+\beta}}\right)(1 - \sin\overline{\alpha+\beta})^2 \, d\beta,$$

$$ds_{13} = -2\pi l \sin\alpha \, . \, dl.$$

By eliminating $d\beta$ and dl, and using the fact that the

radius of the surface, R, is given by $\dfrac{l \sin \alpha}{(2 \cos \alpha + \beta)}$, it follows

that $\qquad dv_{12} = \dfrac{R}{2} \ ds_{12} + \dfrac{R}{2} \cos \beta \ ds_{13}$,

which is the special case of (1) for a spherical surface. Comparison with (1) gives (4)—with $K = \dfrac{2}{R}$ — and (8) again.

An interesting property of a physical surface in a cylindrical capillary may be mentioned. During a movement of the pistons a particle anywhere in the surface will have a movement normal to the surface superposed on its Brownian movement. The centre of curvature of the (spherical) surface is therefore an instantaneous centrifugal centre. The lines of flow will therefore be tractrices ; the axis of the cylinder will make an intercept of constant length (equal to the radius of curvature) on the tangent to any one of these tractrices.

The authors would like to thank B. Higman for his helpful suggestions.

Summary.

The relationship of a proposed thermodynamic definition of surface tension to the properties of a " physical " surface described anywhere within the interphase between two phases has been considered. It has been found that the proposed definition accords with previous conceptions of surface tension.

References.

(1) See refs. (1), (2), and (3) of paper IV., which immediately precedes this paper.

XXXI. *A Note on Paramagnetism of the* Mn++ *Ion in the* S *State. By* S. S. BHATNAGAR, *D.Sc. (Lond.), F.Inst. Phys.,* M. B. NEVGI, *M.Sc., and* R. L. SHARMA, *B.Sc. (Hons.)* *.

THE paramagnetism of Mn++ ion has been extensively studied both theoretically and experimentally. The notable experimental workers in this field are Honda [1], Owen and his collaborators [2], Cabrera [3],

Theodorides [4], Duperier [5], Jackson [6], Foex and Brunet [7], Krishnan [8], Valayos [9], and Bose [10]. Amongst the theoretical workers Bethe, Van Vleck [11], and Penney [12] are important. The ions Mn^{++} and Fe^{+++} differ from others of the iron group in that they are in ^6S state, and so devoid of any angular momentum. In the case of Mn^{++} the theory leads to the result that the Weiss constant θ appearing in the well-known relation

$$\chi_M = \frac{CM}{T-\theta}$$

is zero. The susceptibilities of this ion at various temperatures correspond to the simple Curie law of inverse dependence on absolute temperature. This result has been fully verified experimentally by Jackson and others, but there are evidences in the other direction which show some deviation from this rule. According to these deviations the values of θ are 24 to 28 for Mn ion in $MnCl_2$ and 22 to 27 for that in $Mn(NO_3)_2$. Recently Bose has pointed out that θ is less than 3 in the above cases. The present investigation was undertaken to settle this controversy by carrying out the magnetic measurements on the manganese salts of organic acids, which can be obtained in a fine state of purity and are devoid of molecular complexities which exist in many inorganic salts.

Experimental.

The apparatus employed during this investigation is a modified form of Gouy's balance. For higher temperature measurements an electric oven made of mica pieces and nicrom wire was used. In order to avoid the changes in the field that might perhaps be produced near the pole pieces the readings for the standard substances were repeated at higher temperatures, and were found to be the same as those at the lower temperatures. In order to see whether the substances in the tube had attained the temperature recorded by the thermometer in the electric furnace anhydrous copper sulphate and cobalt sulphate were tried, and from the Curie-Weiss law

$$\chi_M = \frac{C_M}{T-\theta}$$

the values of temperature were calculated.

TABLE I.

Substance.	Temperature calculated.	Temperature observed.
Copper sulphate (anhydrous) ...	89·4° C.	90° C.
Cobalt sulphate (anhydrous)....	89·6° C.	90° C.

The agreement between the observed and the calculated values of temperatures justifies the above assumption.

Calculations were made according to the equation

$$\frac{\omega_{p_1}}{\omega_{p_2}} = \frac{\chi_{p_1} m_{p_1} - \chi_a m_{a p_1}}{\chi_{p_2} m_{p_2} - \chi_a m_{a p_1}}$$

or

$$\chi_{p_2} = \frac{1}{m_{p_2}} \left[(\chi_{p_1} m_{p_1} - \chi_a m_{a p_1}) \frac{\omega_{p_2}}{\omega_{p_1}} + \chi_a m_{a p_2} \right],$$

where χ_{p_1}=specific susceptibility of the standard substance;

χ_{p_2}=specific susceptibility of the specimen;

ω_{p_1}=pull due to the standard substance;

$\omega_{p_2}=$,,   ,,   specimen;

m_{p_1}=mass of the standard substance;

$m_{p_2}=$,,   ,,   specimen;

$m_{a p_1}$=mass of the air displaced by the standard substance;

$m_{a p_2}$=mass of the air displaced by the specimen.

In most theoretical discussions it is convenient to use the Weiss magneton and the Bohr magneton numbers; the former is denoted by P and the latter by P_B. The values of P and P_B are calculated from the equations

$$P = 14·06\sqrt{\chi_M(T-\theta)}$$

and

$$P_B = 2·839\sqrt{\chi_M(T-\theta)},$$

or

$$\frac{P}{P_B} = \frac{14·06\sqrt{\chi_M(T-\theta)}}{2·839\sqrt{\chi_M(T-\theta)}} = 4·952.$$

The substances used were B.D.H. guaranteed extra pure substances. The anhydrous compounds were prepared from these substances by careful heating until all the water of crystallization had been driven out, as shown by the constancy of the weight of the material and the agreement of the loss in weight with that corresponding to the loss of the contained molecules of water.

Experimental Results.

TABLE II.

Susceptibilities at Different Temperatures.

Substance.	Temp. °C.	Specific suscepti- bility. $\chi \times 10^{-6}$.	Molecular suscepti- bility. $\chi_M \times 10^{-6}$.	Ionic suscepti- bility. $\chi_{Mn^{++}} \times 10^{-6}$.
Manganese acetate (anhydrous).	32	75·75	13105	13163
	70	67·30	11643	11701
	122	58·88	10186	10244
Manganese formate (anhydrous).	32	92·18	13366	13400
	70	82·32	11936	11970
	122	70·61	10238	10272
Manganese lactate (anhydrous).	32	57·13	13311	13404
	70	50·08	11668	11761
	122	43·90	10229	10323
Manganese oxalate (anhydrous).	32	93·21	13329	13357
	70	82·94	11860	11888
	122	71·50	10224	10252

Discussion of Results.

From the close examination of the results obtained many important points may be brought forth. The magneton numbers obtained in Mn salts and Mn^{++} ion are nearly the same. Many authors have found corrections for anions unnecessarily, as it can be seen that these corrections are negligible for most paramagnetic substances. In order to determine the magneton number all that is needed is a study of the paramagnetic property at three or more temperatures.

Sommerfeld [13], taking advantage of the inferences as to the simple types of the term splitting in Zeeman effect, assumed that the resolved moment of an atom whose moment was " b " Bohr magneton could only take the values b, $(b-2)$, $(b-4)$ . . . . $-b$. This modification leads to the expression

$$P_B = \sqrt{b(b+2)}$$
$$= \sqrt{5(5+2)} = \sqrt{35} = 5·916;$$

$\because \qquad b = 5$ for Mn^{++},

$\therefore \qquad P = 5·916 \times 4·952 = 29·3.$

Similarly, the appropriate expression for an ion in an arbitrary $^r L_j$ state was given by Hund [14] as

$$P_B = g\sqrt{j(j+1)},$$

where g is the Landé's splitting factor.

When the resultant moment of an atom is due entirely to spin, g value is 2. Therefore for S states Hund's expression reduces to

$$\sqrt{4S(S+1)}.$$

TABLE III.

Author.	Substance.	P.
Experimental :		
Bose	$MnCl_2$.	28·8
Bose	$Mn(NO_3)_2$.	28·5
S. Valayos	$MnSO_4$.	28·99
Jackson	$MnSO_4 . 5H_2O$.	29·4
,, ...	$MnSO_4 . 4H_2O$.	29·0
,, ...	$MnSO_4 . (NH_4)2SO_4 . 6H_2O$.	29·2
K. S. Krishnan	Mn.	29·9
Foex and Brunet	$MnCl_2$.	28·0
,, ,, ...	$MnSO_4$.	29·0
,, ,, ...	$Mn_2P_2O_7$.	30·0
A. Duperier	Mn.	28·06
Cabrera	Mn.	29·3
Theodorides	$MnSO_4$,	29·0
Present authors	$(CH_3COO)_2Mn$.	28·21
,, ,, ...	$(CH_3 . CH(OH) . COO)_2Mn$.	28·30
,, ,, ...	$(H . COO)_2Mn$.	28·37
,, ,, ...	$\begin{matrix} COO\diagdown \\ \mid \quad Mn. \\ COO\diagup \end{matrix}$	28·27
Theoretical :		
Hund	—	29·30
Sommerfeld	—	29·30

TABLE IV.

Magneton Values of Mn++ and Mn Salts.

Substance.	Temp. °C.	P for salt.	P for Mn++.	P_B for salt.	P_B for Mn++.
Manganese acetate (anhydrous).	32	28·10	28·21	5·67	5·69
	70	28·09	28·16	5·67	5·68
	122	28·20	28·27	5·69	5·70
Manganese formate (anhydrous).	32	28·26	28·40	5·70	5·73
	70	28·40	28·40	5·73	5·73
	122	28·30	28·31	5·71	5·71
Manganese lactate (anhydrous).	32	28·26	28·40	5·70	5·73
	70	28·12	28·12	5·67	5·67
	122	28·26	28·39	5·70	5·73
Manganese oxalate (anhydrous).	32	28·26	28·26	5·70	5·70
	70	28·26	28·26	5·70	5·70
	122	28·24	28·29	5·70	5·71

The spectroscopic state of Mn^{++} is $^6S_{5/2}$,

$$\therefore \quad P_B = 2\sqrt{5/2(5/2+1)}$$
$$= 5 \cdot 916,$$
and $$P = 29 \cdot 3.$$

This is equivalent to Sommerfeld's expression. In the preceding table magneton values both experimental and theoretical are given.

In finding out the Weiss and Bohr magneton values only the Curie law has been utilized. This shows that the simple Curie law holds good in the case of Mn^{++}.

References.

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(2) Owen, Sci. Rep. Tohoku Univ. (13 onwards).
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(6) L. C. Jackson, Phil. Trans. Roy. Soc. London, ccxxvi. A, p. 107 (1926).
(7) G. Foex and A. Brunet, *Compt. Rend.* clxxxiv. pp. 443–445 (1927).
(8) K. S. Krishnan, *Z. Physik*, lxxi. pp. 131–140 (1931).
(9) S. Valayos, *Annals Soc. esp. fis. quim.* xxxi. p. 597 (1933).
(10) A. Bose, ' Nature,' cxxxiii. p. 213 (1934).
(11) Van Vleck, ' Theory of Electric and Magnetic Susceptibility Chapter II.
(12) W. G. Penney, Phil. Mag. xvii. p. 961 (1934).
(13) Sommerfeld, *Zeit. f. Phys.* xl. p. 333 (1926).
(14) Hund, *Zeit. f. Phys.* xxxiii. p. 855 (1925).

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XXXII. *Notices respecting New Books.*

Intrinsic Geometry of Ideal Space. By A. R. FORSYTH, Sc.D., LL.D., Math.D., F.R.S. [Two volumes, 1200 pages.] (Macmillan : Price £6 6s. 0d.)

IN a handsome volume of over five hundred pages Prof. A. R. Forsyth, in 1912, published his 'Lectures on the Differential Geometry of Curves and Surfaces,' where he dealt with the usual topics of differential geometry in space of three dimensions on a generous scale of treatment. In 1930 appeared ' Geometry of Four Dimensions,' from the pen of the same author, in two large volumes of some five hundred pages each, dealing to a big extent with the same theme from a more extended standpoint. Finally, there has just appeared ' Intrinsic Geometry of Ideal Space,' in two volumes of some six hundred pages each. The whole subject has been developed in the grand manner, and Professor Forsyth has laid mathematicians of all types under a deep debt of gratitude for bringing this most important field of geometry within easy

access of all who for any reason wish to reach in as convenient and comprehensive a way as possible the latest results.

In Volume I. the first chapter is purely introductory; Chapter II. deals with " general amplitudes " ; Chapter III. with " curvatures of geodesics in free general amplitudes " ; Chapter IV. with " geodesic properties relative to the tangent homaloid " ; Chapter V. with " Riemann's measure of curvature of an amplitude " ; Chapter VI. with " sub-amplitudes in a general amplitude " ; Chapter VII. with " primary general amplitudes " ; Chapter VIII. with " free surfaces " ; Chapter IX. with " ranges on surfaces and the Riemann measure of curvature " ; Chapter X. with " parallel geodesics on free surfaces " ; Chapter XI. with " curvatures of geodesics on surfaces " ; Chapter XII. with " curves of curvature on a surface " ; Chapter XIII. with " parametric curves on a surface " ; Chapter XIV. with " free regions " ; Chapter XV. with " torsion, tilt, coil of regional geodesics."

Volume II. opens with Chapter XVI., which treats of " surfaces in a region and geodesics on a regional surface." Chapter XVII. deals with " surfaces geodesic to a region " ; Chapter XVIII. with geodesic parallels in a region ; Chapter XIX. with geodesic parallelograms, geodesic cells, in a region ; Chapter XX. with parametric curves in a region ; Chapter XXI. with regions and some special problems ; Chapter XXII. with orthagonal surfaces, minimal surfaces, in a region ; Chapter XXIII. with free domains and the circular curvature of geodesics ; Chapter XXIV. with domainal geodesics, gremial curvatures ; Chapter XXV. with domainal geodesics, non-gremial properties ; Chapter XXVI. with geodesic triangles and the sphericity of a domain in a superficial orientation ; Chapter XXVII. with regions in a domain, geodesic regions ; Chapter XXVIII. with curvatures of geodesics in domainal regions ; Chapter XXIX. with domainal surfaces, surfaces geodesic to the domain ; Chapter XXX. with domainal curvatures of surfaces ; Chapter XXXI. with some properties of primary domains ; Chapter XXXII. with geodesic parallels in a domain ; Chapter XXXIII. with parametric curves in a domain.

It might be expected that the ordinary mathematical reader of general interests and competent power would get overwhelmed, or at all events bewildered, in reading through this vast field of connected theory. Such is, however, by no means the case. Even an honours student at the university while pursuing his normal course could, if he is willing to put the necessary trouble into his effort, work his way intelligently through these volumes. Differential geometry is largely a subject in itself, and does not in general call for the use of other subjects as " tool " subjects. The immature student is not therefore handicapped by having

incessant recourse to the theorems of other branches of mathematics. It is true that in some parts of the present work a knowledge of Invariants and of Differential Equations would facilitate progress and understanding, but the appeal to these ancillary branches of mathematics is neither extensive nor profound. There does exist, however, some decidedly heavy approximative work, but it is perfectly straightforward, and will repay the labour of going through it, though many readers will go straight to the result itself and take the proof as read.

For readers who are interested in "comparative mathematics" there are some delightful sections. In ordinary elementary geometry, for example, a parallelogram can be defined as having its opposite sides equal, or its opposite sides parallel, or its opposite angles equal, and such definitions are equivalent. To ordinary straight lines in a plane correspond geodesics on a surface, and the author introduces this part of his subject thus :—

"When the theory of parallels on a surface comes to be discussed, there will arise the necessity of considering figures, bounded by four geodesic arcs and analagous to parallelograms in a plane : they will be called geodesic parallelograms. It will appear, however, that there are various types of such figures, each type associated with some specific property of a plane parallelogram ; and though the plane properties always lead to the same unique plane parallelogram, it will be found that the corresponding geodesic properties do not lead to a geodesic parallelogram, which is the same for all." The parallelograms of Levi-Civita, Pérès, etc. are then discussed. This is, from the general reader's standpoint, first - rate mathematical work. He is taken back to the very simplest elements of the subject, which he had come to regard as self-evident and inevitable, and the prop of inevitability begins to creak and totter. Or, again, a well-known theorem is extended. Thus, the area of a spherical triangle on a sphere of radius R is $R^2 \times$ (the spherical excess of the triangle). The extension is that the area of a geodesic triangle is equal to $\frac{1}{K} \times$ (the angular excess of the triangle), where K is the *sphericity* of the amplitude at the point under consideration in the superficial orientation defined by the two geodesics drawn through this point.

Enough has been said to indicate the general character and scope of the work. The charm of the exposition itself can be gauged only by the perusal of this new work, which possesses all the quality that one has learned to expect from the mathematical treatises of Prof. Forsyth.

[The Editors do not hold themselves responsible for the views expressed by their correspondents.]

FIG. 7.

FIG. 8.
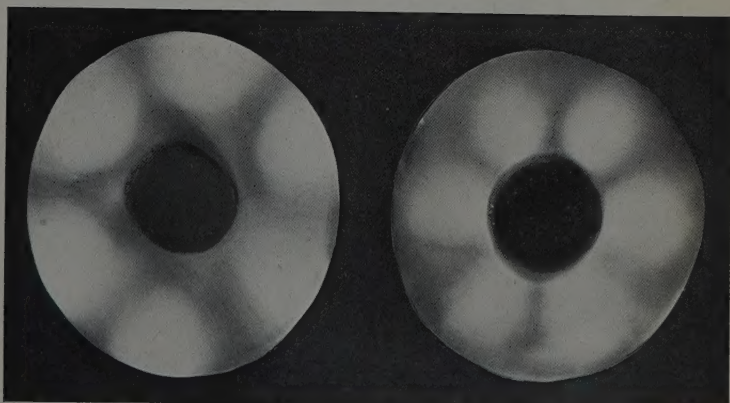
(a).   (b).

Hollow quartz cylinders in oscillation viewed between nicols.